

Advances in
**ORGANOMETALLIC
CHEMISTRY**

VOLUME 15

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Advances in Organometallic Chemistry

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Recent Developments in Theoretical Organometallic Chemistry

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I

INTRODUCTION

The general availability of high-speed computers and the realization that orbital symmetry effects can exert a profound influence on the stereochemical course of organic reactions (67, 74, 75, 209, 242, 244) have resulted in a very rapid and extensive development of theoretical organic chemistry during the last 10 years. The discovery that certain metal ions could catalyze some organic pericyclic reactions that had been classified as orbitally "forbidden" (149, 231) has prompted several attempts to extend the Woodward-Hoffmann rules to organometallic chemistry (91, 142, 143, 175, 179, 221, 225). The role of metal ions in such reactions is still being debated, and, in general, orbital symmetry arguments as applied to organometallic reactions have not had that predictive quality that characterized their application to organic reactions. This debate has highlighted, nevertheless, the need to understand more clearly the bonding in organometallic complexes and in addition the perturbations introduced by ligand dissociation and polytopal rearrangement processes. During the last 2 years, some very accurate molecular orbital calculations on crucial organometallic complexes have been reported which have given a clearer picture of the nature of the

metal-olefin bond (15, 193), and there have been some illuminating analyses of the factors influencing the geometries of organometallic complexes particularly by Hoffmann and his co-workers (78, 118, 119, 134, 190). Therefore, the stage seems well set for some interesting advances in theoretical organometallic chemistry.

When reviewing recent developments in theoretical organometallic chemistry, I have tried not to place too much emphasis on the development of computational techniques. Some authors claim that, given enough time and money, complete and reliable *ab initio* computations will be made for large molecules containing transition metals. Thus, the need for simplified schemes and concepts such as conventional chemical bonds, which are considered only special features of a more delocalized model (69), will automatically be ruled out. Nevertheless, the experimental work of chemists is still based on bonds, atoms, simplified pictorial models of orbital interactions, and generalized rules concerning stable electronic configurations, e.g., Hückel's and the inert gas rule. No amount of sophisticated computer output will encourage a synthetic chemist to abandon these fundamental tools of the trade. In my view, the drive to develop more sophisticated theoretical computer-based models must be accompanied by the search for generalizations and simplified bonding schemes that can be used by the bench chemist and readily taught to new generations of chemists. This philosophy has greatly influenced the structure and tone of this review.

The first section summarizes simply the essential features of the different types of molecular orbital calculations currently used to solve theoretical problems in organometallic chemistry. A critical comparison of these calculations is also given. The second section discusses the bonding in organometallic complexes and draws on recent computational results and develops the chemical and structural implications of bonding models based on perturbation theory arguments.

II

TYPES OF MOLECULAR ORBITAL CALCULATIONS

A. Linear Combination of Atomic Orbitals Methods

Application of LCAO-MO ideas to transition metal complexes faces no special restrictions (13, 17, 25, 37, 69, 236). Molecular orbitals Φ_i are expressed as linear combinations of 1-electron atomic wave functions,

χ_p , on the various atoms in the molecule in the following way:

$$\Phi_j(i) = \sum_{p=1}^m c_{pj} \chi_p(i) \quad (1)$$

In *semiempirical* calculations expression (1) is limited to the valence shell atomic orbitals of each atom. Thus, for a first-row element, such as iron, only the $3d$, $4s$, and $4p$ wave functions would be included in the calculation. In *ab initio* (or parameter-free) self-consistent field (SCF) calculations, a more complete set of basis atomic functions is used including inner shell orbitals. The weight of chemical evidence suggests that a detailed consideration of inner shells should not be necessary to most chemical properties, but it appears to be difficult to remove them from the atomic orbital basis set without having a drastic effect on the energies of the resulting valence molecular orbitals. Murrell and Harget (164, 165) have suggested that this approximation fails because, in the absence of the inner-shell orbitals, the valence atomic orbitals do not have the radial nodes of SCF atomic orbitals. In addition, the energies of atomic orbitals with the same principal quantum number but different l quantum numbers (e.g., $2s$ and $2p$) are underestimated in valence shell approximations.

Except for 1-electron atoms, atomic orbitals are not simple functions of the distance between the electron and the nucleus. Accurate wave functions are generally expressed as a linear combination of simple algebraic functions. The most convenient functions from which to build up accurate atomic orbitals are the Slater orbitals (28, 29, 206):

$$\chi_{nlm}(k,r) = N r^{n-1} \exp(-kr) Y_{lm}(\theta,\phi) \quad (2)$$

where n is an integer that corresponds to the principal quantum number, and $Y_{lm}(\theta,\phi)$ are the spherical harmonic functions that describe the angular variation of the orbital.

An alternative set of functions used to build up atomic orbitals are Gaussian functions that have a radical dependence $\exp(-kr^2)$. A linear combination of these functions gives a reasonable representation of an atomic orbital. The functions are used for computational expediency in *ab initio* calculations, because four-center Gaussian integrals can be reduced to two-center integrals, which are relatively easy to calculate on a computer (21).

The c_{pj} coefficients of the molecular orbitals $\Phi_j(i)$ in Eq. (1) are obtained

by solving the familiar set of homogeneous equations:

$$\sum_{q=1}^m c_{qj}(H_{pq} - S_{pq}e_j) = 0 \quad (p = 1, 2, \dots, m) \quad (3)$$

and obtaining the eigenvalues e_j for the molecular orbitals. Matrix elements S_{pq} and H_{pq} are electronic integrals that depend on the atomic wave functions χ_p and χ_q . The overlap integrals S_{pq} ,

$$S_{pq} = \int \chi_p^* \chi_q d\tau$$

may be evaluated from the algebraic expressions for the atomic wave functions. Integrals H_{pq} are matrix elements of an effective Hamiltonian:

$$H_{pq} = \int \chi_p^*(i) H_{\text{eff}}(i) \chi_q(i) d\tau_i \quad (4)$$

The Hamiltonian, H_{eff} , which is called the Hartree-Fock-Roothan operator is a 1-electron operator whose application yields the energy of an electron moving in the average field of the other electrons and nuclei. In principle an SCF theory approach will lead to a well-defined expression for H_{eff} for closed and open shell systems (188, 189), and with the aid of modern computers H_{pq} integrals can be evaluated numerically even for transition metal complexes. This type of *ab initio* calculation has been reported for a reasonable number of organometallic complexes of first-row transition elements by Hillier, Veillard, and their co-workers (48, 49, 102, 103, 111–115; 58, 68, 70, 187, 228, 229).

In Fenske and Hall's *parameter-free* SCF calculations (80–84), the H_{eff} 1-electron operator is substituted by a model 1-electron operator that has a kinetic energy and potential energy term for each atomic center in the complex. This approach assumes that the electron density may be assigned to appropriate centers. The partitioning of electron density is done through Mulliken population analyses (163) until self-consistency is obtained. The Hamiltonian elements are evaluated numerically, and the energies of the MO's depend only on the choice of basis functions and the internuclear distance.

In the extended Hückel or Wolfsberg-Helmholtz approximations, only the valence orbitals are included in the basis set and the Hamiltonian elements are estimated from ionization potential and spectral data for the free atoms (or ions). The diagonal elements H_{pp} are estimated from valence state ionization energies of the atomic orbitals χ_p , and the off-diagonal elements H_{pq} are calculated on the basis of an average of the diagonal elements H_{pp} and H_{qq} and weighted according to the overlap integral S_{pq} . Several formulas have been recommended for this averaging

process, and the more commonly used ones are shown below (13, 63, 116, 241, 243):

$$H_{pq} = kS_{pq}(H_{pp} + H_{qq})/2 \quad (5)$$

$$= kS_{pq}(H_{pp}H_{qq})^{1/2} \quad (6)$$

$$= \frac{kS_{pq}(H_{pp}H_{qq})}{(H_{pp} + H_{qq})/2} \quad (7)$$

Constant k is usually assigned a value of 1.75 to 2.00. Normally, the valence state ionization energies are corrected for charge effects and the calculations cycled to self-consistency (13). Madelung correction terms have also been included by some workers (109).

The complete neglect of differential overlap (CNDO) method has been widely applied in organic chemistry. Basically, it is an SCF method in which the integrals are not calculated but are parameterized. The method has the advantage that it is very quick and yet successfully accounts for the geometric and spectroscopic properties of organic molecules (164). It has not been widely applied to organometallic molecules, and the reader is referred to papers by Perkins and Armstrong (7, 136, 137) and Kato (126, 196) for the type of parameterization used when metal atoms are involved (see also Ref. 64).

B. Self-consistent Field- X_α -Scattered-Wave Calculations

An attractive alternative to the Hartree-Fock SCF procedures described in the preceding section has been developed in recent years by Slater (207) and Johnson (121). In X_α calculations, molecular orbitals of a molecule are not generated from linear combinations of analytical orbitals in the traditional Hartree-Fock manner but are generated simply from the numerical partial-wave solutions of Schrödinger's equation for well-defined spherical regions within the molecule and its immediate environment. The SCF- X_α technique is based primarily on the division of a molecule (or an infinite solid) into component polyatomic aggregates. Each aggregate, which may be an entire polyatomic molecule, part of a macromolecule, or a polyatomic complex in an ordered or disordered solid, is geometrically partitioned into atomic, interatomic, or extramolecular spherical regions. The Schrödinger equation is numerically integrated within each region in a partial-wave representation for spherically averaged and volume averaged potentials. These wave functions (and their first derivatives) are then joined to embrace the

whole molecule by multiple scattered-wave (SW) theory. The effects of a particular environment on the aggregate are described by boundary conditions. The procedure leads to a set of rapidly convergent secular equations that are solved numerically for the molecular orbital wave functions and their energies. The matrix elements of these equations are simple to evaluate in comparison with those characteristic of *ab initio* LCAO methods because there are no multicenter integrals.

Generally, the atomic, outer, and interatomic sphere radii are chosen so as to minimize the volume between the spheres. Other physical considerations, such as empirical atomic or ionic radii, can also influence the initial choice of sphere sizes. It has also been recently shown that overlapping spheres may be used since the various expansion theorems are still valid (192). This technique has been used to calculate the molecular orbitals of Zeise's salt and ferrocene discussed later in this review (191, 193).

C. Comparison of Theoretical Models

From the foregoing brief survey, it is clear that there is not a consensus of opinion on the valence model most suitable for dealing with theoretical problems in organometallic chemistry. The type of calculation chosen in part reflects the prejudices of individual theoretical chemists, but more importantly it is tempered by the aims of specific research projects. Theoretical research aims may be classified into the following broad classes: (1) interpretation of specific spectroscopic measurements; (2) rationalizing and predicting molecular geometries; (3) accounting for the stereochemical pathways and rates of organometallic reactions; and (4) the development of generalized bonding schemes and conceptual frameworks. Each of these aims makes different demands on the theoretical model and, therefore, the different approaches will be compared with reference to the specific aims.

1. Interpretation of Spectroscopic Measurements

Historically, crystal field theory was the first theoretical model (11, 86, 101, 123) used to explain *d-d* transition energies in metal complexes. Its usefulness is restricted to those complexes whose bonding is largely ionic, and its major deficiency arises from its inability to account for charge transfer transitions. The iterative extended Hückel and the *ab initio*, limited basis set, Hartree-Fock calculations are capable of de-

scribing this type of transition, but each has its own set of disadvantages.

The iterative extended Hückel type of calculation has been widely used, especially by Gray and his co-workers (13) to interpret the visible and ultraviolet spectra of transition metal complexes, but from a quantitative point of view it has not proved to be very reliable. This difficulty arises primarily because the theory is based on a 1-electron Hamiltonian and, therefore, neglects important electron repulsion effects.

In *ab initio* calculations, these terms are not neglected and the agreement between observed and calculated electronic transition energies is expected to be better. However, for *ab initio* calculations the number of integrals that have to be computed increases as a fourth power of the number of basis set orbitals used. Therefore, to make such calculations practicable for transition metal systems, limited basis sets have to be used for all but the most simple of molecules. The critical choice of basis set can, it seems, affect the energies of the calculated molecular orbitals and even their relative orderings. This problem has been highlighted by two recent *ab initio* calculations on $[\text{Ni}(\text{CN})_4]^{2-}$ using basis sets of different quality (70, 115).

Comparable calculations based on the X_α -scattered-wave method require a fraction of the time and generally seem to give results that are quantitatively more satisfactory. A more detailed comparison of the *ab initio* and scattered-wave methods as applied to transition metal complexes has been given in a recent review by Johnson (121). The degree of accuracy that can be attained using the scattered-wave- X_α method can be judged from the observed and calculated electronic transition energies given in Table I for ferrocene. The agreement for both *d-d* and charge-transfer energies is excellent (191).

A further problem associated with *ab initio* Hartree-Fock calculations applied to transition metal complexes is the apparent invalidity of Koopmans's theorem. The basic assumption of Koopmans's theorem (131), which states that the 1-electron orbital eigenvalues of a ground-state calculation are related to the ionization potentials of the molecule, is that the distribution of the electron density of the remaining electrons in the positive ion (formed in the ionization process) is essentially unchanged from that in the neutral parent molecule. Although the shortcomings of this theorem, which also ignores electron correlation and relativistic effects, are well known, its widespread use in band assignments of ionization processes in terms of ground-state molecular orbitals of the neutral parent molecule has provided a convenient and comprehensible description of the molecule's electronic structure. For

TABLE I
COMPARISON OF ORBITAL TRANSITION ENERGIES CALCULATED BY THE SCF- X_α -SW
METHOD WITH EXPERIMENTAL VISIBLE AND ULTRAVIOLET SPECTRAL DATA

Orbital transition	Type of transition	SCF- X_α -SW Transition energy (191) ($\times 10^{-3} \text{ cm}^{-1}$)	Experimental ^a ($\times 10^{-3} \text{ cm}^{-1}$)
$8a_{1g} \rightarrow 5e_{1g}$	<i>d-d</i>	20.5	21.8 18.9 } 20.4
$4e_{2g} \rightarrow 5e_{1g}$	<i>d-d</i>	25.2	30.8 24.0 22.4 20.9 } 24.5
Charge transfer			
$6e_{1u} \rightarrow 5e_{1g}$	L \rightarrow M	36.5	37.7
$8a_{1g} \rightarrow 4e_{2u}$	M \rightarrow L	39.2	41.0
$4e_{2g} \rightarrow 4e_{2u}$	M \rightarrow L	43.9	42.8
$6e_{1u} \rightarrow 9a_{1g}$	L \rightarrow M	47.1	47.5
$6e_{1u} \rightarrow 5e_{2g}$	L \rightarrow LM	50.1	49.5
$5e_{1u} \rightarrow 5e_{1g}$	L \rightarrow M	53.9	—
$3e_{2u} \rightarrow 5e_{1g}$	L \rightarrow M	55.1	51.6
$6a_{2u} \rightarrow 5e_{1g}$	L \rightarrow M	55.5	—

^a Taken from Refs. 5, 211, and 212.

organometallic π -complexes, the orbital relaxation effects that accompany ionization appear to be significant and very dependent on the precise nature of the molecular orbital involved. Therefore, it is necessary to recalculate the orbital energies for the positive ion formed in the ionization process. This is usually done by a restricted Hartree-Fock method (113). In Table II the ionization potentials calculated for ferrocene on the basis of an *ab initio* calculation are compared with the experimentally determined photoelectron energies. The ionization energies based on Koopmans's theorem are clearly unsatisfactory, and the results are greatly improved when the difference in total energies of the molecule and the positive ion is taken (58).

Koopmans's theorem is not valid for X_α calculations, but Slater's transition state concept applies. This approximation allows the interpretation of electronic transitions in terms of 1-electron orbitals and yet includes electronic relaxation effects (208). The virtual (unoccupied) orbitals of X_α theory have a physical significance and can be used to discuss excitations of the electronic system, because the same potential due to the $N - 1$ other electrons affects both occupied and unoccupied

orbitals. This view contrasts with the Hartree-Fock theory according to which occupied orbitals experience a potential due to $N - 1$ other electrons, whereas an unoccupied orbital experiences a potential more appropriate to N other electrons.

Table II also shows the calculated ionization energies for ferrocene based on the SCF-SW- X_α procedure. The X_α calculation gives a better quantitative account of the observed photoelectron spectrum than the *ab initio* calculations of Veillard *et al.* (58). Whether the X_α technique is generally more reliable remains to be established.

The above discussion has focused on the interpretation of electronic and photoelectronic spectral measurements that reflect directly the relative order of the highest occupied and lowest unoccupied molecular orbitals within a molecule. Traditionally, however, the bonding in transition metal carbonyl and olefin complexes has been discussed on the basis of infrared spectral measurements. It has long been assumed that when ligands such as CO coordinate to a transition metal, then the reduction in the stretching frequency (or more correctly the force constant) of the ligand is directly related to the degree of back donation to the ligands π^* -antibonding levels. Fenske and his co-workers (39, 80,

TABLE II
COMPARISON OF IONIZATION POTENTIALS OF FERROCENE CALCULATED BY THE SCF- X_α TRANSITION STATE PROCEDURE AND THE SCF-LCAO METHOD

	SCF- X_α -SW transition state (191) (eV)	Hartree-Fock SCF-LCAO method (58) (eV)		Experimental (eV)	
		^a	^b	Ref. 79	Ref. 184
$8a_{1g}$	7.9	10.1	16.6	6.858	6.88
$4e_{2g}$	8.5	8.3	14.4	7.234	7.23
$6e_{1u}$	9.3	11.1	11.7	8.715	8.72
$4e_{1g}$	9.7	11.2	11.9	9.38	9.39
$5e_{1u}$	11.5	—	—	—	—
$3e_{1g}$	11.6	—	—	—	—
$3e_{2u}$	11.6	15.5	16.0	12.2	12.3
$3e_{2g}$	11.7	—	—	—	—
$6a_{2u}$	11.7	—	—	—	—
$7a_{1g}$	12.8	—	—	13.0	—
$5a_{2u}$	14.2	—	—	—	—
$6a_{1g}$	14.6	—	—	13.6	13.46
$2e_{2u}$	16.0	—	—	—	—
$2e_{2g}$	16.1	—	—	16.4	16.5

^a Difference in total energies of molecule and ion.

^b Koopmans's theorem result.

81) have completed an important molecular orbital analysis of the factors influencing the C–O stretching force constants [as calculated by the Cotton-Kraihanzel method (57)] in the complexes $M(CO)_5L$. The calculations are based on the parameter-free, approximate Hartree-Fock method discussed briefly above. This molecular orbital study indicated that in complexes $M(CO)_5L$ the carbonyl orbital populations remained essentially constant and equal to those of free CO except for the highest occupied (5σ) and lowest unoccupied ($2\pi^*$) levels. Therefore, in every complex studied, the electronic distribution of the coordinated carbonyl ligand could be described by the following electronic configuration:

$$(1\sigma)^2(2\sigma)^2(3\sigma)^2(1\pi_x)^2(1\pi_y)^2(5\sigma)^a(2\pi_x^*)^b(2\pi_y^*)^b$$

The 5σ level is primarily located on the carbon atom and can be identified with the carbonyl lone pair orbital, but in addition it is somewhat antibonding between carbon and oxygen. The population of this orbital has a significant influence on the carbonyl stretching force constant and, therefore, changes in the carbonyl force constant cannot be assigned solely to back donation effects. Force constants k in the $M(CO)_5L$ molecules can be described by the following equation:

$$k(md/A) = 36.42 - 11.76(2\pi^*) - 9.93(5\sigma)$$

where $2\pi^*$ and 5σ are the electron occupancies of these orbitals as determined by a Mulliken population analysis. From this equation it is clear that σ and π effects contribute almost equally to the observed force constant changes. There have also been some analyses of force constant data in the complexes $Cr(CO)_3(\eta\text{-arene})$ based on extended Hückel calculations by Brown and his co-workers (31).

2. Molecular Geometry

The N^4 computational problem noted above for *ab initio* calculations becomes a severe handicap for solving organometallic molecular structure problems. Even for a simple study of a particular distortion mode of a transition metal complex involving a single angle change, the molecular energy has to be calculated for several points along the distortion coordinate before the energy minimum can be accurately located. Using current Hartree-Fock *ab initio* calculations, this type of theoretical analysis could take several hundred hours on a modern computer.

The X_α -SW technique does not suffer from this deficiency because the calculations do not involve multicenter integrals and converge rapidly to a final solution. Johnson (121) has noted that this method is suitable for solving geometric problems, and the high quality of the

results which seem to have been obtained to date are certainly most encouraging. The lack of widespread application of this method, however, must lead us to give the Scottish verdict of "not proven" at this stage in its development.

The extended Hückel type of calculation has been widely used recently [especially by Hoffmann and his co-workers (78, 118, 119, 134), Cusachs (166, 167, 237), and the author (118, 154)] to discuss the observed geometries of coordinated ligands. As noted above, the absolute energies of molecular orbitals obtained from these calculations are probably somewhat inaccurate due to the neglect of the inner-shell orbitals. They do reflect, nevertheless, important maximum overlap criteria and broad electronegativity effects. These factors coupled with the high speed of these calculations (even for relatively large asymmetric organometallic molecules) make the extended Hückel calculation most suitable for molecular structure problems and especially those related to angular changes in the molecule. Cusachs and his co-workers have discussed various criteria for judging the probable equilibrium geometry in metal-olefin complexes (166, 167, 237), e.g., total energy, and maximum overlap populations. Extended Hückel calculations are less satisfactory for analyzing the effects of bond length changes in molecules (116).

In situations where maximum overlap criteria are important, it is often possible to construct simple perturbation theory arguments to account for broad geometric trends. Burdett has illustrated in a very neat fashion how the geometries of binary metal carbonyls $M(CO)_n$ may be rationalized using such an angular overlap model (35). The same problem has also been tackled by Elian and Hoffmann using more complete extended Hückel calculations (78).

3. Organometallic Reaction Pathways

There have been very few quantitative or semiquantitative theoretical analyses of reaction pathways for organometallic reactions. Some analyses have been made of the olefin insertion reaction, which is an important feature of Ziegler-Natta catalysts (8, 51) and the β -elimination process (197) using CNDO type of calculations. The soluble Ziegler-Natta catalysts based on $M(\eta-C_5H_5)_2$ metal ligand moieties have also been considered from an extended Hückel point of view (134). Clearly, the study of possible reaction pathways requires a large number of related calculations and makes *ab initio* calculations prohibitively expensive. The reliability of the foregoing semiempirical type of calculations for this purpose is difficult to assess. It should be noted, however, that

even the simplest type of calculation can give the experimental chemist a rough idea of the charge distribution in the molecule and the nodal characteristics of the frontier orbitals which seem to be so important in deciding the reactivities and reaction pathways of molecules. This type of information treated in an experimental vein can be most useful for synthetic chemists planning new experiments (24, 25, 30).

As noted previously, the outstanding success of orbital symmetry rules in organic chemistry (75, 242) has led to many attempts to extend these rules to organometallic chemistry and metal-catalyzed processes. These qualitative analyses based on the principle of conservation of orbital symmetry or second-order Jahn-Teller effects have been reviewed extensively (91, 142, 143, 173, 175, 179, 221, 225) and will not be considered in any detail here.

4. Development of New Conceptual Frameworks

The course of modern organometallic chemistry has been greatly influenced by three simple generalizations: the Dewar-Chatt-Duncanson synergic bonding model for metal-olefin complexes (40, 72); Pauling's electroneutrality principle (174), and the 18-electron or inert gas rule (202). In this section the impact of recent theoretical calculations on these important generalizations will be evaluated.

Recent SCF- X_α -SW (193) and *ab initio* (15) calculations have confirmed that the essential features of the Dewar-Chatt-Duncanson model are correct, and these calculations will be discussed in more detail in Section III,A below. The importance of metal-ligand back donation for stabilizing polyene metal tricarbonyl (48) and sandwich complexes (58) has also been confirmed. Underlying the Dewar-Chatt-Duncanson model is Pauling's powerful electroneutrality principle stating that the final charge on the central atom in a complex will lie between $+1/2$ and $-1/2$. Recent *ab initio* calculations have confirmed that in high oxidation state complexes, e.g., MnO_4^- , the high formal charge on the metal is greatly reduced and approximates to that suggested by the electroneutrality principle (see Table III).

For organometallic complexes that have a low formal oxidation state, e.g., $\text{Ni}(\text{CO})_4$ and $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_6)$, a less consistent picture has emerged from recent *ab initio* calculations. The calculated charges for the metal-carbonyl and -nitrosyl complexes $\text{Ni}(\text{CO})_4$, $\text{Co}(\text{CO})_3(\text{NO})$, and $\text{Fe}(\text{CO})_2(\text{NO})_2$ lie between 0 and +1 (see Table III), but for the π -complexes $\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)$, $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_6)$ and sandwich complexes $\text{Cr}(\eta\text{-C}_8\text{H}_8)_2$ the calculated metal charges are surprisingly high, i.e., +1.4 to +2.7. At the present time, it is difficult to say whether

TABLE III
CHARGES CALCULATED ON THE CENTRAL METAL ATOM
IN INORGANIC AND ORGANOMETALLIC COMPLEXES
BASED ON *ab Initio* CALCULATIONS

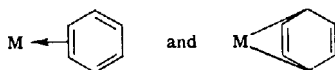
Complex	Calculated metal charge	References
MnO_4^-	+0.93	49
CrO_4^{2-}	+0.58	49
VO_4^{3-}	-0.07	49
$\text{Ni}(\text{NO})(\eta\text{-C}_5\text{H}_5)$	+0.82	115
$\text{Ni}(\text{CO})_4$	+0.50	113
$\text{Co}(\text{CO})_3(\text{NO})$	+0.60	113
$\text{Fe}(\text{CO})_2(\text{NO})_2$	+1.00	113
$\text{Mn}(\text{CO})_5\text{CH}_3$	+1.23	102
$\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_6)$	+1.46	48
$\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)$	+2.08	103
$\text{Cr}(\eta\text{-C}_6\text{H}_6)_2$	+2.66	103
$\text{Ni}(\eta\text{-allyl})_2$	+1.86	228, 229

these charges are an artifact of the Mulliken population analysis used to calculate them (163), a peculiarity of Hartree-Fock calculations on metal π -complexes, or actually a reflection of chemical reality.

The 18-electron rule has played an important role in rationalizing the structures and reactivities of a wide range of organometallic complexes of the transition metals (219), but its simplicity and aura of numerological certainty have obscured the fact that it has little quantum-mechanical justification. Craig and Doggett (59) in a rare theoretical analysis of the problem concluded that the rule will be followed when the metal-to-ligand charge transfer supplements electron donation from the ligand—for it is then that the radial and angular parts of the potential experienced by the metal d orbitals approaches that of the next rare gas element. Other workers have noted that the rule reflects the complete utilization of metal valence shell orbitals (145).

Hoffmann and Elian's broad analysis of the bonding capabilities of metal carbonyl fragments $\text{M}(\text{CO})_n$, (78), based on extended Hückel calculations have demonstrated how the total number of available orbitals for these fragments varies with n . Their analysis of the variation is closely connected to the 18-electron rule. Each metal atom has nine orbitals: $5d$, $1s$, and $3p$. In an ML_n complex, each ligand carries a σ -donor orbital that finds among the set of nine metal orbitals a partner with which to interact. The result is that n of the nine metal orbitals are destabilized by σ -bonding with the ligands leaving $9-n$ orbitals to either

hold metal d electrons or act as acceptor orbitals of the fragment. The spatial extent, hybridization, and energies of the $9-n$ valence orbitals of the ML_n fragment are very sensitive to the geometric arrangement of the ligands L . For geometries related to the octahedral parent, the fragments "remember" the low-energy position of the octahedral t_{2g} set, stabilized by interaction with the π^* -orbitals of the carbonyls, and as a consequence have $6-n$ valence orbitals. Utilization of these frontier orbitals leads naturally to a fulfillment of the 18-electron rule. Mingos (156–158) has related the topological properties of the bonding networks in polyhaptometal–olefin complexes to the 18-electron rule using perturbation molecular orbital theory ideas first developed for aromatic hydrocarbons (73, 74, 140, 209). This method has proved most useful for distinguishing the relative stabilities of isoelectronic isomers, e.g.,



These types of analyses based as they are on perturbation theory arguments are at present most suitable for seeking out generalizations. The slowness of *ab initio* calculations and the difficulty of interpreting physically the results of SCF- X_α -SW calculations makes them less suitable for this type of research project.

III

SURVEY OF RECENT THEORETICAL RESULTS

A. Ethylene and Substituted Ethylene Complexes

Dewar (72) and Chatt and Duncanson's (40) elucidation of the bonding in metal–olefin π -complexes coincided almost precisely with the discovery of ferrocene (127, 150, 239) and provided a flexible theoretical framework for the rapid growth of organometallic π -complex chemistry which followed the discovery of that novel compound. This synergic bonding model has been used to rationalize many trends in the structural, chemical, and spectroscopic properties of metal–olefin complexes (96, 106, 107, 110, 183), and its essential features are generally accepted. Recently, sophisticated *ab initio* molecular orbital calculations have been reported for Zeise's salt $K[PtCl_3(C_2H_4)]$ (193) and the complex ion $[Ag(C_2H_4)]^+$ (15), giving a very detailed picture of the metal–olefin bond

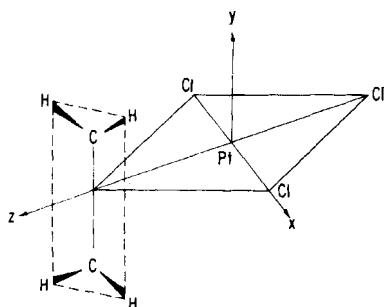


FIG. 1. Coordinate system and geometry of Zeise's anion.

and confirming the essential features of the Dewar-Chatt-Duncanson model.

The SCF- X_α -SW calculation on Zeise's salt, based on the C_{2v} molecular geometry shown in Fig. 1, represents the most accurate theoretical study to date. The most striking feature of the analysis is the degree to which the ethylene is preserved as a subunit within the complex. The π -orbital of ethylene makes the most significant contribution to metal-olefin bonding by mixing with the platinum d orbitals that have the correct symmetry transformation properties, i.e., d_{z^2} and $d_{x^2-y^2}$ (see Fig. 1 for a definition of the axis system referred to). Contour plots of the relevant orbitals shown in Fig. 2 indicate a significant degree of mixing of the d_{z^2} and $d_{x^2-y^2}$ orbitals. This type of mixing is a common feature of transition metal complexes with C_{2v} symmetry (118) and has the effect of removing some antibonding electron density from the z to the y axis. Readers familiar with the classic Chatt-Duncanson bonding picture will identify these metal-olefin interactions with the forward donation component of that model. It does appear, however, that these authors overestimated the degree of involvement of the metal $6s$ and $6p$ orbitals in metal-olefin bonding. Presumably for this platinum(II) complex the large $d \rightarrow s$ and $d \rightarrow p$ promotion energies (169) prevent the formation of idealized dsp^2 hybrid orbitals on the platinum atom as originally proposed.

The SCF- X_α -SW calculation also confirms the importance of the back donation component of this model, and a contour plot of the relevant molecular orbital is shown in Fig. 3. Johnson and his co-workers (193) have estimated that this component may contribute up to 25% of the total metal-olefin bond energy. These calculations have given a more satisfactory account of the electronic absorption characteristics of this

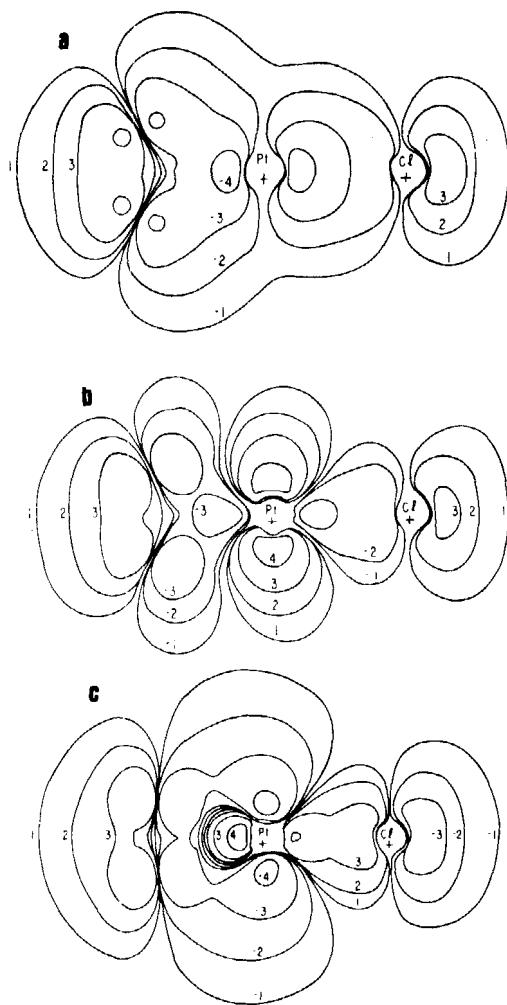


FIG. 2. Contour plots of σ -like bonding orbitals of Zeise's anion. The contour values increase in absolute magnitude with increasing absolute values of the contour labels. The sign of the labels gives the sign of the orbital lobes. The set of contour values plotted is the same for each of the three orbitals. The interior nodes at the various atoms are not shown for clarity of presentation: (a) the $5a_1$ orbital, (b) the $6a_1$ orbital, and (c) the $7a_1$ orbital showing significant interaction between the ethylene π -orbital and the Pt $d_{x^2-y^2}$ orbital. [Reproduced from Rösch *et al.* (193), by permission of the American Chemical Society.]

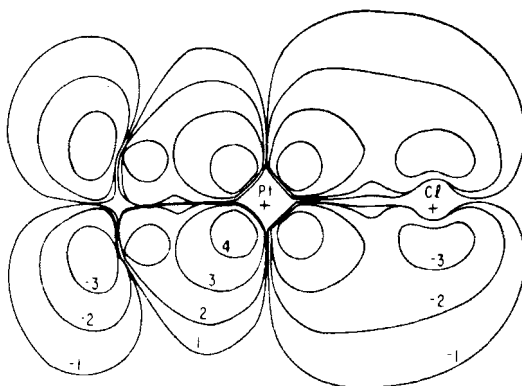


FIG. 3. Contour plot of the π -like bonding orbital of Zeise's anion. The set of contour values are the same as those in Fig. 2. This is the $2b_2$ orbital. [Reproduced from Rösch *et al.* (193), by permission of the American Chemical Society.]

ion (71, 193) than those based on more approximate semiempirical calculations (126, 161, 198, 200).

These authors have also suggested that the strong metal-olefin bonding in Zeise's salt is accompanied by a weakening of the *trans*-platinum chlorine bond, because the molecular orbitals that contribute to the chlorine electron density sphere have mainly nonbonding characteristics. Accurate X-ray and neutron diffraction studies (105, 120) have shown that the *trans*-platinum chlorine bond length [2.327(5) Å] is only marginally longer than the average of the *cis* bonds [2.305(7) Å], and therefore this bond weakening effect does not seem to show up in the ground-state properties of this salt. The kinetic lability of the *trans*-chlorine is well documented (16, 106, 107).

Armstrong *et al.* (6) have examined *trans* influences and *trans* effects (180) in complexes $[\text{PtXCl}_3]^-$ and $[\text{PtX}(\text{NH}_3)\text{Cl}_2]$ ($\text{X} = \text{C}_2\text{H}_4, \text{PH}_3, \text{CO}, \text{H}_2\text{S}, \text{NH}_3, \text{H}_2\text{O}, \text{H}^-, \text{CN}^-, \text{CH}_3^-, \text{Br}^-, \text{Cl}^-, \text{OH}^-, \text{and NO}_2^-$) using modified CNDO molecular orbital calculations. They concluded that if π -bonding is possible in the proposed trigonal bipyramidal transition state for nucleophilic substitution (16), then the π -bonded ligand dictates the stereochemical course of the reaction. For a σ -donor ligand, both its *trans* influence and its ability to act as a donor in the transition state are important, but the former predominates when the two effects do not reinforce each other. These calculations, therefore, support earlier proposals by Chatt (41) and Orgel (170) for *trans* effects in platinum(II) complexes. Gray (95), Mason (141), and Drago (245) have also dis-

cussed trans effects and influences in square-planar platinum(II) complexes from a molecular orbital point of view.

Chemical considerations suggest that metal-olefin back donation will be less important for silver(I) than for platinum(II), and Basch's *ab initio* calculations on $[\text{Ag}(\text{C}_2\text{H}_4)]^+$ (15) have confirmed this view. These calculations suggest that most of the electronic rearrangement of the ethylene unit in this complex ion can be accounted for by the polarization effects induced by the positive charge on the silver atom. Indeed, the bonding metal-olefin molecular orbital has only 6.5% Ag 5s orbital character. This result agrees nicely with recent ESR studies on γ -irradiated silver-olefin complexes which estimate a 5s spin density of 4.6% for this molecular orbital (92, 93).

The foregoing analysis suggests an interesting trend that is relevant to an understanding of ^{13}C chemical shifts in metal-olefin complexes. There is a pronounced increase in the carbon 2s orbital population when the olefin coordinates to the silver ion, which is consistent with the shift to higher field of the ^{13}C resonance of the complexed ligand (172). Basch also examined the interesting possibility suggested by Urch (224) that the olefin might bond to silver in the edgewise manner shown in Fig. 4 and concluded that this geometry was energetically highly unfavorable.

Since it has been established that the essential features of the Dewar-Chatt-Duncanson model are consistent with the most sophisticated calculations to date, we can now focus attention on the geometrical, thermodynamic, and chemical implications of the perturbation theory model. Perturbation theory (within the approximation of zero intermolecular overlap) suggests that first-order intermolecular interaction between occupied molecular orbitals will leave the energy of the system unchanged but that interaction between a filled molecular orbital with an empty molecular orbital of the same symmetry will lead to a first-order stabilization. This stabilization is inversely proportional to the energy difference between the molecular orbitals. As a consequence, the primary interactions between an unsaturated organic molecule and a metal ion will be dominated in general by the energies of the highest occupied (HOMO) and lowest unoccupied (LUMO) molecular orbitals

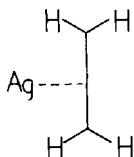


FIG. 4. Geometry for silver ethylene complexes proposed by Urch (224).

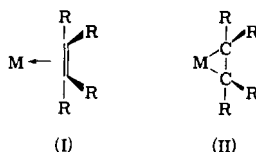
of these molecular entities (74, 117, 124). The development of the orbital symmetry rules of organic chemistry have largely followed from the realization of the crucial roles played by the HOMOs and LUMOs in the transition states of reactions (75, 89, 90, 94, 199, 242), but the applications of these perturbation theory ideas to organometallic chemistry are still at an early stage in their development.

1. Structures of Metal-Olefin Complexes

Accurate structural analyses on metal-olefin complexes during the last 10 years (14, 106, 147, 162, 195) have suggested the following generalizations.

a. Coordination of the olefin leads to an increase in the C—C bond length. The observed increase is sensitive to the oxidation state of the metal and the electron-donating properties of the other ligands and can be as large as 0.2 Å.

b. The olefin substituents bend away from the metal on coordination so as to give a quasi-tetrahedral character to the coordination atoms. This observation added to the long-standing discussion as to whether the metal-olefin bond is better represented by valence structure I or II.



c. The coordinated olefins show definite conformational preferences with respect to the coordination plane defined by the metal and the other ligands. Thus, in Zeise's salt and other platinum(II) complexes, the olefin carbon-carbon bond axis is orthogonal to the platinum-ancillary ligand plane (see Fig. 1). In the trigonal d^{10} complexes (Fig. 5) and trigonal bipyramidal d^8 complexes (Fig. 6), the olefin axis is coplanar to within a few degrees with the idealized trigonal coordination plane (147, 162, 195).

Several years ago, it was shown that the geometrical effects noted in the preceding generalizations a to c are a direct consequence of the symmetry restrictions imposed by the Dewar-Chatt-Duncanson model (151, 152). The bond length increase could originate through either σ -bond (ligand \rightarrow metal) or π -bond (metal \rightarrow ligand) charge transfer. Moreover, one would expect the relative importance of these processes to reflect the formal oxidation state of the metal with the olefin acting as a net Lewis base in, say, a platinum(II) complex and a net Lewis acid in

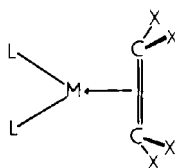


FIG. 5

FIG. 5. Geometries of the zero-valent platinum metal-olefin complexes, e.g., $[\text{Pt}(\text{PR}_3)_2(\text{olefin})]$.

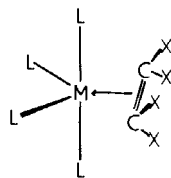


FIG. 6

FIG. 6. Geometries of d^8 -olefin complexes, e.g., $[\text{Fe}(\text{CO})_4(\text{olefin})]$ and $[\text{IrCl}(\text{CO})(\text{PR}_3)_2(\text{olefin})]$.

a platinum(0) complex. X-Ray crystallographic studies have shown that the mean platinum(II)-carbon(olefin) bond length is approximately 0.1 \AA longer than the platinum(0)-carbon(olefin) value, and, since the σ -covalent radius of platinum(II) must be somewhat smaller than that of platinum(0), it carries the implication of substantial back donation from platinum(0). The strong π -basicity of zero-valent metal fragments accounts for the long C—C bond lengths in their olefin complexes and is reflected in the metal binding energies as measured by electron spectroscopy for chemical analysis (ESCA) studies (14, 50, 148).

Blizzard and Santry (19) investigated changes in the C—C—H bond angles of the uncoordinated acetylene ligand as a function of the electronic population of the acetylene π^* -orbital and concluded that the observed cis-bent geometry in transition metal-olefin and -acetylene complexes is a direct consequence of synergic bonding effects. Extended Hückel calculations on model platinum olefin and acetylene complexes (166, 167, 237) have confirmed that the degree of bending

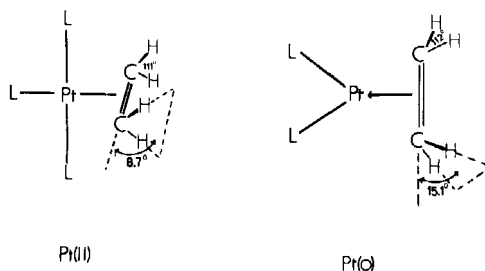


FIG. 7. Calculated equilibrium geometries for platinum(II) and platinum(0) complexes. [Taken from Nelson *et al.* (167).]

back is sensitive to the formal oxidation of the metal. The calculated equilibrium geometries for two such complexes are shown in Fig. 7. There does not seem to be a simple relationship between the increase in the carbon-carbon bond length following coordination of substituted olefins and the deformation of the bond angle described above. Fluoroolefins show the largest distortions, yet photoelectron (34) and UV studies (18) have shown that these ligands do not have particularly low-lying π^* -levels. This anomaly could arise either from a high sensitivity to distortion for this type of orbital or the predominance of overlap terms that are not calculated explicitly in the Dewar-Chatt-Duncanson model. This observation is relevant to an understanding of the stabilities of metal-olefin complexes and will be discussed in more detail below.

The conformation of the olefin with respect to the metal-ligand coordination plane in olefin complexes reflects the unequal back donation abilities of the metal orbitals with d_π pseudosymmetry (152, 190). In nonaxially symmetric metal-ligand fragments, the arrangement of the ligands can greatly influence the degree of back donation by encouraging the more favorable admixture of metal d_π and p_π character shown in Fig. 8. This hybridization increases the directional properties of the metal π -donor orbital and raises its energy in such a way that a stronger interaction with olefin π^* -orbital results.

Hybridization is a concept normally associated with the valence bond approach but may also be derived from molecular orbital theory by using second-order perturbation theory in the following way (78, 117, 190).

Consider the simplified interaction diagram for an angular ML_2 fragment shown in Fig. 9. In the formal scheme of setting up the interaction between the metal d_{xz} and p_x orbitals and the antisymmetric combination of ligand orbitals, the metal-ligand mixing takes place in first order and will give rise to the usual bonding and antibonding molecular orbitals; however, the intermixing of metal orbitals (hybridization) will only occur as a second-order effect. The sign of mixing of p_x

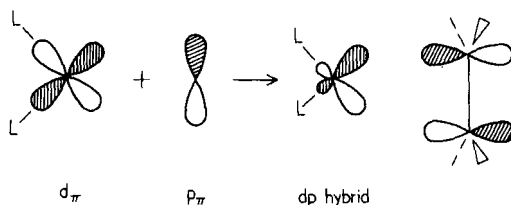


FIG. 8. d_π - p_π hybridization effects in angular ML_2 fragments that encourage more effective metal-olefin back donation.

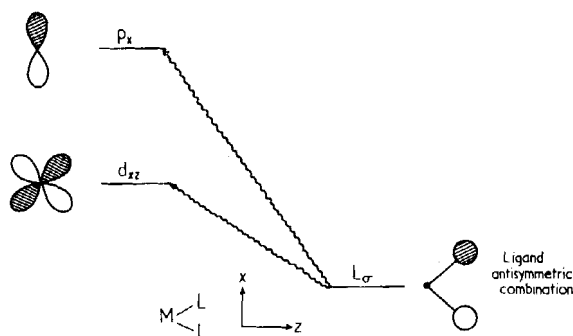


FIG. 9. Interaction diagram for the antisymmetric orbitals of the angular ML_2 fragment.

into d_{xz} will be determined by the matrix element:

$$\frac{\langle d_{xz}|L\rangle \langle L|p_x\rangle}{(E_{xz} - E_L)(E_{xz} - E_x)} \quad (8)$$

where $L = (1/2^{1/2})(\phi_1 - \phi_2)$, i.e., the antisymmetric combination of ligand orbitals. If the interaction overlaps are chosen to be positive as they are shown in the Fig. 9, then the numerator in expression (8) is positive. The sign of expression (8) is determined by the energy denominator. From the level ordering $E_L < E_{xz} < E_x$, the sign of expression (8) is negative for the donor orbital of the ML_2 fragment and, therefore, p_x (with the phase defined in Fig. 9) mixes into d_{xz} with a minus sign. This results in hybridization away from ligands L in the manner shown in Fig. 8.

The degree of hybridization (and, therefore, the degree of back donation to the olefin) will be influenced by the $L-M-L$ bond angle, because the numerator in expression (8) depends on the $\langle xz|L\rangle$ and $\langle L|x\rangle$ overlap terms. Indeed, when this angle is 180° the intermixing will be zero, for at this angle the $\langle xz|L\rangle$ overlap term will be exactly zero (Fig. 10). For a T-shaped ML_3 fragment, the degree of hybridization will also be zero for similar reasons (Fig. 11).

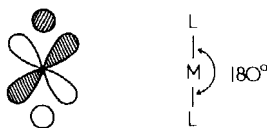
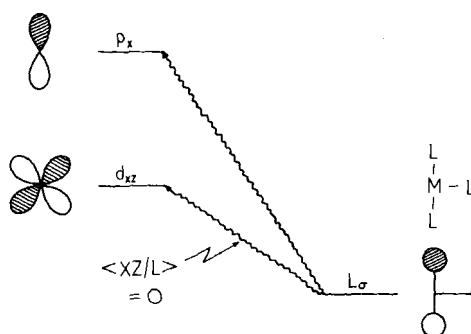
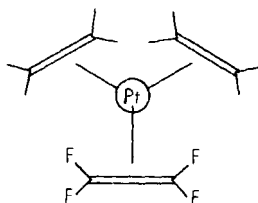


FIG. 10. Illustration of the zero overlap between $(1/2^{1/2})(\phi_1 - \phi_2)$ orbital combination and d_{xz} orbital for linear $L-M-L$ fragment.

FIG. 11. Interaction diagram for a T-shaped ML_3 fragment.

From the above analysis it is clear that angular ML_2 fragments provide a better π -back-donation plane than linear ML_2 or T-shaped ML_3 fragments. This perturbation theory analysis provides a simple explanation for the observation that the olefin lies in the trigonal plane in the d^{10} and d^8 complexes shown in Figs. 5 and 6. For Zeise's salt, neither of the symmetry distinct donor planes have ligand arrangements that would encourage effective $d_{\pi}-p_{\pi}$ hybridization effects. In such a complex, the equilibrium geometry is probably determined by steric rather than electronic effects, and low-energy barrier for olefin rotation is anticipated and is, indeed, observed (9, 62, 104).

The preceding perturbation theory analysis is supported by extended Hückel calculations by Cusachs and his co-workers (166, 167, 237) on model platinum(II)- and platinum(0)-olefin and -acetylene complexes and Hoffmann and Rossi's extensive analysis of five-coordinate transition metal complexes (194). By using similar arguments, Hoffmann and Rösch (190) predicted that the planar conformation would be energetically preferred for d^{10} $M(C_2H_4)_3$ complexes. This geometry has now been established by Stone (214) and his co-workers for the platinum-olefin complex shown in Fig. 12.

FIG. 12. Geometry established by X-ray crystallographic studies for $[Pt(C_2H_4)_2(C_2F_4)]$ (214).

As indicated above the degree of hybridization in d^{10} $[ML_2(\text{olefin})]$ complexes should be sensitive to the $L-M-L$ angle. This effect should be reflected in the geometry of the olefin and X-ray crystallographic studies of complexes $[Pt(\text{olefin})(PPh_2(CH_2)_mPPh_2)]$, where the $L-M-L$ angle could be systematically varied by changing the number of methylene groups, CH_2 , and thus allow this theoretical point (171) to be tested.

2. Stabilities of Metal-Olefin Complexes

The stabilization energy, δE , resulting from metal-olefin bonding may be estimated from the following perturbation theory expression (220):

$$\delta E = A/\Delta_\pi + B/\Delta_\pi^* \quad (9)$$

where A and B involve geometric and overlap terms, and Δ_π and Δ_π^* represent the HOMO-LUMO energy separations implicit in the Dewar-

TABLE IV
IONIZATION POTENTIALS AND $\pi \rightarrow \pi^*$ TRANSITION ENERGIES FOR OLEFINS^a

Olefin	IP ^b (eV)	$\pi \rightarrow \pi^*$ ^c (eV)	$-E_\pi^*$ (eV)
Fumaronitrile	11.15	5.64	5.51
Acrylonitrile	10.91	6.43	4.48
Methyl vinyl ketone	10.10	5.95	4.15
Styrene	8.47	4.33	4.14
1-Hexene	9.46	7.00	2.46
Vinyl acetate	9.19	6.1	3.1
<i>trans</i> -Stilbene	7.95	3.71	4.24
$CH_2=CHO(CH_2)_3CH_3$	8.93	6.43	2.50
<i>trans</i> -2-Hexene	9.13	6.84	2.29
<i>cis</i> -2-Hexene	9.13	6.98	2.15
2-Methyl-1-pentene	9.12	6.58	2.54
$CH_3CH=C(CH_3)_2$	8.67	6.98	1.69
C_2H_4	10.52	7.28	3.24
C_2F_4	10.52	8.88	1.64
$CH_2=CHF$	10.58	7.44	3.14
$CH_2=CHCl$	10.00	6.4	3.6
Propylene	9.73	7.10	2.63
1-Butene	9.58	7.10	2.48
$CHF=CF_2$	10.53	7.61	2.92
<i>trans</i> - $CHF=CHF$	10.38	7.28	3.10

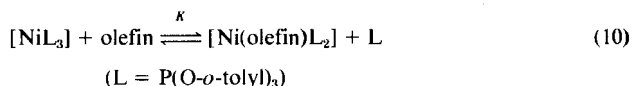
^a Data taken from Tolman (220).

^b Ionization potential, adiabatic if available.

^c Separation of energy levels from UV spectra.

Chatt-Duncanson synergic bonding model and estimated from ionization potential and electronic spectral data. Ideally the Δ_π and Δ_π^* energy terms would be based on the energies of the π - and π^* -olefin levels for the equilibrium geometry observed in the complex, but, as this information is not generally available, the energies of these levels in the free ligand are used (220, 34, 18). The HOMO and LUMO of the metal-ligand fragment may be similarly estimated from the ionization potential of the free atom and spectroscopic data for the parent metal-ligand complex.

Generally, the energy of the olefin π^* -level is more sensitive to substituent effects than the π -level (see Table IV for example). Therefore, often a simple plot of the equilibrium constant for the metal-olefin complex vs the energy of the lowest unoccupied olefin molecular orbital gives a reasonable straight-line graph. Such a plot reported by Tolman (220) for the equilibrium



is shown in Fig. 13. Tolman noted that only conjugated olefins, e.g., styrene and *trans*-stilbene and fluorinated olefins $\text{C}_2\text{H}_n\text{F}_{4-n}$ show major departures from the idealized behavior expected for this simple theoretical analysis.

It is commonly believed that fluoroolefins form more stable com-

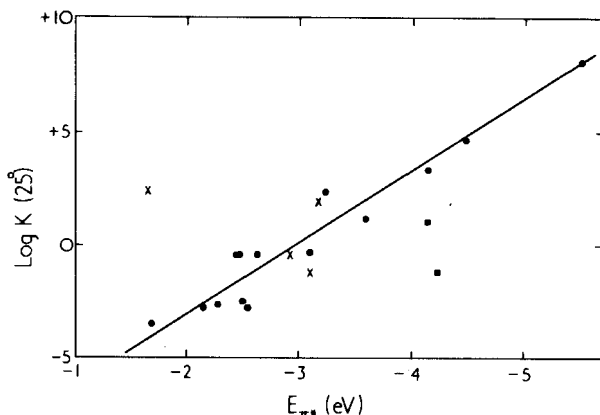
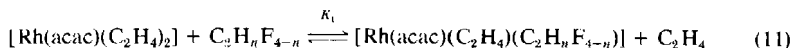
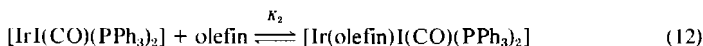


FIG. 13. Correlation of $\log K_1$ (25°) with the energy of the lowest unoccupied orbital of the free olefin. The $\text{C}_2\text{H}_{4-n}\text{F}_n$ olefins are designated by crosses and $\text{C}_2\text{H}_{4-n}(\text{C}_6\text{H}_5)_n$ by squares [Reproduced from Tolman (220), by permission of the American Chemical Society.]

plexes with metals than olefins with hydrocarbon substituents, but the current thermodynamic evidence on this point is ambiguous. Cramer's study (60) of the equilibrium



showed that vinyl fluoride ($K_1 = 0.32$) and vinylidene fluoride ($K_1 = 0.10$) form less stable complexes than ethylene. Only with C_2HF_3 ($K = 88$) and C_2F_4 ($K = 59$) were the fluoroolefin complexes more stable than the unsubstituted derivatives. Stronger metal- C_2F_4 bonding vis à vis metal- C_2H_4 bonding in rhodium complexes was also indicated by a bond length comparison in $[\text{Rh}(\eta\text{-C}_5\text{H}_5)(\text{C}_2\text{H}_4)(\text{C}_2\text{F}_4)]$ (104). For the equilibrium



Vaska (227) showed that K_2 was 100 times larger than for C_2F_4 than C_2H_4 .

Tolman's study of the equilibrium [Eq. (10)] showed that none of the simple fluorinated olefins $\text{C}_2\text{H}_n\text{F}_{4-n}$ were as good as C_2H_4 in coordinating to the nickel phosphite complex $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$.

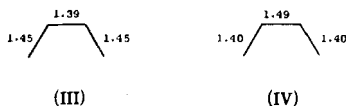
Very strong metal-fluoroolefin bonding has also been inferred from preparative studies and the similarity of geminal ^{19}F - ^{19}F coupling constants in fluoroolefin complexes to those found in fluorinated cyclopropanes (61, 85, 215).

Recent photoelectron (34) and UV spectral studies (18) on fluorinated olefins have demonstrated that their lowest-lying π^* -levels are higher than the π^* -level of ethylene itself, whereas their highest-lying π -levels are essentially at the same energy as the ethylene π -level (see Table IV). Therefore, if the stability of the metal-olefin complexes is correlated simply with the energy of the fluoroolefin π^* -level in accordance with the simple perturbation theory analysis, then their stability constants are grossly underestimated (see Fig. 13). Tolman has suggested that this apparent failure of the perturbation approach arises from using electronic spectral data appropriate for the planar D_{2h} olefin. By severely bending back the fluorines from the plane containing the C—C axis, the π^* -orbitals of the fluorinated olefins may drop sufficiently to allow a strong interaction with the occupied metal orbitals. The fluorines in fluorinated olefin complexes are generally bent back to a greater extent than other substituents (e.g., CN), and Tolman has argued that the structural reorganization required before the olefin can bond effectively may be responsible for the slowness of its reaction with $\text{Ni}[\text{P}(\text{O}-o\text{-tolyl})_3]_3$. The use of electronic spectral data on the parent planar olefins

is apparently much more appropriate for the other olefins that are bent back to a lesser degree.

B. Butadiene Complexes

(1,4- η -Butadiene)tricarbonyliron and other dienetricarbonyl complexes have played an important part in the development of theories of bonding between transition metals and unsaturated hydrocarbons. The early structural results were summarized by Churchill and Mason (44) and were provided with an explanation in terms of the "excited state" model (141, 144). The essential point of this model is that the geometry of butadiene is modified on coordination in such a way that the C—C bond lengths are more closely related to the geometry of the first excited state (III) rather than the ground state (IV). A recent structural survey of butadiene-metal-tricarbonyl complexes by Cotton *et al.* (55) has confirmed that the central C—C bond of the coordinated butadiene ligand is indeed 0.02 Å shorter than the outer C—C bonds, which have an average bond length of 1.420 Å.



Connor *et al.* (48) have reported an *ab initio* calculation on $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_6)$ indicating that the coordinated butadiene ligand bears a substantial negative charge (-0.88 e) and, therefore, resembles more closely the butadiene anion than an excited state of the free ligand. This charge buildup arises from effective back donation from filled d_π orbitals to the lowest-energy antibonding orbital of butadiene. The nodal characteristics of this orbital are such (Fig. 14) that this electron transfer leads to a shortening of the central C—C bond and a lengthening of the outer bonds in much the same way as that for the first excited state of the free ligand. A CNDO calculation has also been reported for $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_6)$ (176) but its reliability has been questioned (48).

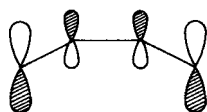
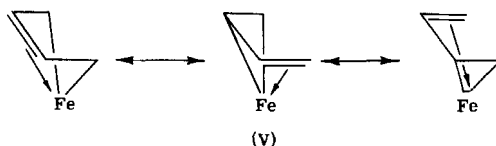


FIG. 14. Nodal characteristics of the lowest-lying π^* -antibonding level of butadiene.

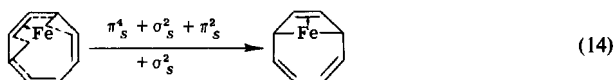
Eliañ and Hoffmann (78) have discussed the different bonding requirements of conjugated and unconjugated dienes and have rationalized the distinct preference shown by the $\text{Fe}(\text{CO})_3$ fragment for conjugated dienes. These extended Hückel calculations have also accounted for subtle changes in the $\text{OC}-\text{M}-\text{CO}$ bond angles that accompany metal fragment-diene bond formation.

Mingos (156-158) has examined the topological properties of the bonding networks generated by the carbon p_π orbitals and the metal d_π orbitals in tetrahapto- and metal-olefin complexes. The phase dislocations introduced by the metal d_π orbitals could perhaps have a crucial effect on the fluxional behavior of these molecules and their cycloaddition reactions with dienophiles. This analysis, based on the perturbation molecular orbital (PMO) method that has been widely used in organic chemistry, also suggests that the following resonance forms give a reasonable description of the bonding in butadiene-iron-tricarbonyl complexes:



This equivalence of the valence bond and molecular orbital descriptions of the bonding in these complexes arises from the *alternant*¹ properties of the metal-butadiene bonding network. A similar equivalence between the two theories occurs for benzene and other polyenes that have alternant π -systems (73, 140).

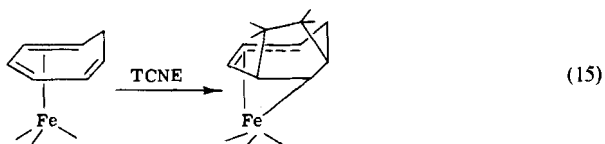
The conventional bond formulas (V) can serve as a useful starting point for discussing the chemical and structural properties of more complex tetrahaptopolyene compounds. For example, the 1,2-sigmatropic shifts of tetrahaptometal-cyclooctatetraene and -benzene complexes may be described in the following ways using Woodward and Hoffmann's topological notations (242):



¹ In an alternant bonding network, the constituent atomic orbitals can be divided into two groups, *starred* and *unstarred*, in such a way that no two orbitals of like parity overlap directly (i.e., are adjacent).

According to the generalized Woodward-Hoffmann rule, the total number of $(4q + 2)_s$ and $(4r)_a$ components must be odd for an orbitally allowed process. Thus, Eq. (14) is an "allowed," and Eq. (13) a "forbidden" sigmatropic rearrangement. The different fluxional characteristics of tetrahapto cyclooctatetraene (52, 138) and substituted benzene (36, 43, 125) metal complexes may therefore be related to orbital symmetry effects.

Tetrahapto cyclohexatriene- and cyclooctatetraene-metal-tricarbonyl complexes undergo some unusual cyclo-addition reactions with tetracyanoethylene in which the dienophile undergoes a 1,3 addition across the coordinated ligand and causes a rearrangement of the metal-carbon bonds, for example (99),



By using the conventional bond formula (V) for the metal butadiene moiety, we may describe this cyclo-addition process as an orbitally "allowed" $\pi_s^2 + \pi_a^2 + \sigma_a^2$ pericyclic reaction (160). (See Fig. 15 for an illustration of the topology of the orbital interactions.)

The topological model described briefly above has also been used to understand the bond lengths in tetrahaptoolefin complexes (156). The calculations have reproduced two important geometric features associated with these complexes, namely the relative insensitivity of the carbon-carbon bond lengths of the coordinated butadiene moiety to the number of phenyl rings fused to it and the fixation of one double bond in the phenyl ring that is adjacent to the butadiene moiety. The observed and calculated bond lengths for two such complexes are shown in Fig. 16, and show a reasonable degree of agreement (156). Similar bond fixation effects have been noted for dihapto- and trihapto-organometallic complexes, e.g., $[\text{Pt}(1,2\text{-}\eta\text{-C}_6(\text{CF}_3)_6)(\text{PEt}_3)_2]$ (33) and $[\text{Mo}(\eta\text{-C}_5\text{H}_5)(\text{CO})_2(1,3\text{-}\eta\text{-benzyl})]$ (133), and may be rationalized in a similar manner using the Hückel molecular orbital model (156).

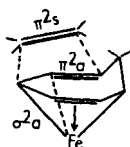


FIG. 15. Topology of the orbital interactions for the cyclo-addition pericyclic transition state of $\text{C}_2(\text{CN})_4 + [\text{Fe}(\text{CO})_3(1,4\text{-}\eta\text{-C}_7\text{H}_8)]$.

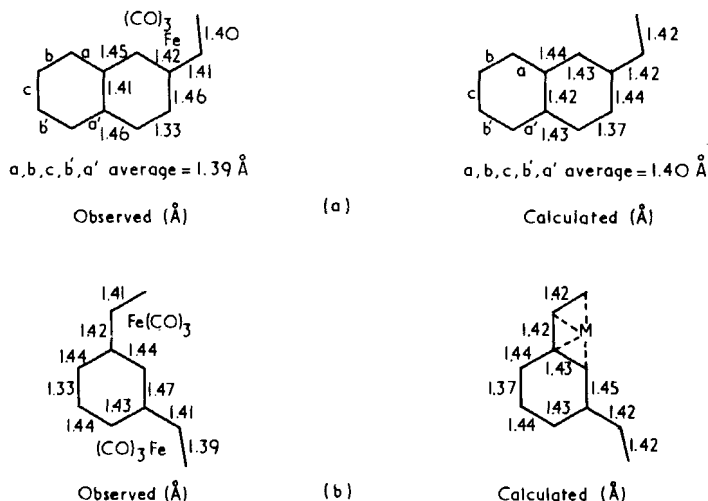
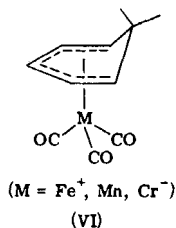


FIG. 16. Observed and calculated carbon-carbon bond lengths for tetrahaptometal-olefin complexes (156), based on a topological Hückel π -bonding model.

C. Pentadienyl Complexes

Two groups have studied the bonding in pentadienyl-metal-tricarbonyl complexes (119, 238) and are agreed that effective overlap between the pentadienyl nonbonding orbital and an orbital of suitable symmetry on the metal (Fig. 17) makes a major contribution to the stability of these complexes. However, the two types of molecular orbital calculation [one an extended Hückel (119) and the other a parameter-free approximate Hartree-Fock calculation (238)] disagree about the precise ordering of energy levels in this type of complex.

In hexadienyl complexes, e.g.,



the six-membered organic ring is highly nonplanar and distorted in such a way that the 5 carbon atoms bonded to the metal form an approximate plane that makes a dihedral angle of approximately 45° with the plane

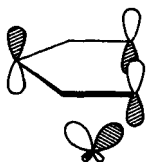
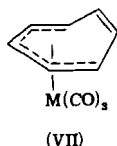


FIG. 17. Primary bonding interaction in pentadienyl-metal-tricarbonyl complexes.

containing the methylene group and the carbon atoms adjacent to it (45). Hoffmann and Hoffman (119) have attributed this distortion to the secondary antibonding interaction between the metal $d-p$ hybrid orbital and the nearer hydrogen $1s$ orbital, as shown in Fig. 18. Alternative explanations based on rehybridization and steric hindrance effects have also been proposed in the literature.

Whitesides *et al.* (238) studied the heptatrienyl complex (VII) and have



attributed its fluxional behavior to the presence of a low-lying π^* -level localized predominantly on the nonbonded *exo*-(double-bond)carbon atoms.

D. Sandwich Complexes

The bonding in metallocenes has been the subject of numerous theoretical and spectroscopic papers (3, 4, 25, 79, 87, 112, 181, 182, 186, 201) and will be discussed only briefly here. A typical simplified

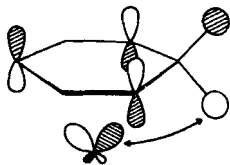


FIG. 18. Secondary antibonding interaction between the metal and the lower methylene hydrogen in hexadienyl complexes.

interaction diagram for a bis(cyclopentadienyl), D_{5d} , metal complex is shown in Fig. 19. The π -orbitals of the two parallel cyclopentadienyl anion rings yield three sets of degenerate orbitals, a low-lying filled pair of a_{1g} and a_{2u} symmetry and a set of filled orbitals e_{1g} and e_{1u} , and a higher-lying empty set, e_{2g} and e_{2u} . These orbitals interact strongly with the metal s and p orbitals that transform according to the symmetry representations, a_{1g} , e_{1u} , and a_{2u} , and in addition a degenerate pair of metal d orbitals, $e_{1g}(d_{xz}, d_{yz})$. The remaining three d orbitals, $a_{1g}(d_{z^2})$, $e_{2g}(d_{x^2-y^2}, d_{xy})$, are essentially nonbonding. Thus, the “ d -level” splitting is

$$e_{2g} \leq a_{1g} < e_{1g} \quad \text{or} \quad (d_{x^2-y^2}, d_{xy}) \leq d_{z^2} < (d_{xz}, d_{yz})$$

In ferrocene, therefore, the nonbonding metal orbitals e_{2g} and a_{1g} are occupied by 6 valence electrons. Some controversy has surrounded the precise ordering of the highest occupied levels in ferrocene. The level ordering $a_{1g} < e_{2g}$ has been inferred from the photoelectron spectrum (79, 184) by using intensity arguments. The first *ab initio* SCF-LCAO calculation resulted in ionization potentials that agreed with the above assignment (58). This ordering was also suggested by earlier simplified molecular orbital treatments (201). The level sequence $e_{2g} < a_{1g} < e_{1g}$ has been inferred from the optical absorption spectrum of ferrocene (211, 212) and supported by recent X_α calculations (191). The calculated transition energies for both the $d-d$ transitions and charge-transfer excitations and the ionizations recorded in the photoelectron spectrum

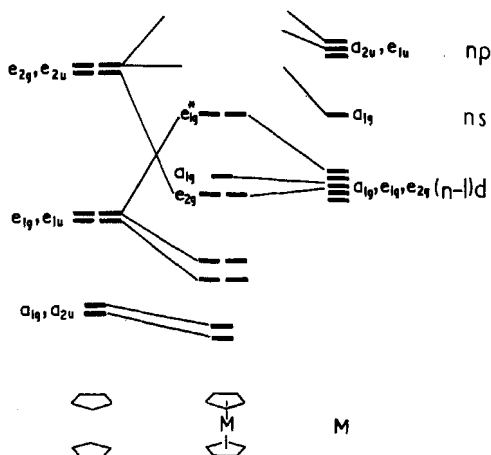
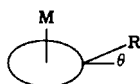


FIG. 19. General interaction diagram for a metallocene with D_{5d} symmetry (134).

are in very good agreement with the observed values (see Section II,C). The apparent disagreement with the photoelectron spectrum has been rationalized by Rösch and Johnson (191) in terms of the small amount of s -orbital character in the a_{1g} orbital that could influence the relative intensities of the photoelectron ionization bands.

Hillier and co-workers (48, 103) have reported *ab initio* calculations on $\text{Cr}(\eta\text{-C}_6\text{H}_6)_2$, $\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)$, and $\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{H}_4)$ and have noted that back donation effects to the ligand's antibonding π^* -levels contribute significantly to the stabilities of these complexes. The low-energy photoelectron spectra of these molecules could only be satisfactorily interpreted when deviations from Koopmans's theorem were taken into account by performing restricted Hartree-Fock calculations on the low-lying ionic states of these molecules.

In sandwich and half-sandwich complexes, the hydrogen atoms (or the substituents) on the cyclopolyene ring do not generally lie in the plane defined by the carbon atoms of the ring. This distortion may be defined by angle θ between the C—R axis and the ring plane shown in structure VIII.



(VIII)

Experimentally, it has been established (20, 76, 185, 223, 226) that for the smaller ring compounds the substituents are bent away from the metal (i.e., θ is negative) and for larger rings the substituents are bent toward the metal (i.e., θ is positive). The crossover between positive and negative θ angles generally occurs for five- or six-membered rings bonded to metals of the first-transition series. Typical θ values are -20° in $[\text{NiCl}(\text{py})_2(\eta\text{-C}_3\text{Ph}_3)]$ (223), -11° in $[\text{Fe}(\text{CO})_3(\eta\text{-C}_4\text{Ph}_4)]$ (76), and $+2^\circ$ in $[\text{Cr}(\text{CO})_3(\eta\text{-C}_6\text{H}_6)]$ (185). Extended Hückel calculations (77) that optimized the θ angle for a series of $\text{M}(\text{CH})_n$ fragments have reproduced this trend. The calculated equilibrium θ values are

fragment:	$\text{Co}(\eta\text{-C}_3\text{H}_3)$	$\text{Fe}(\eta\text{-C}_4\text{H}_4)$	$\text{Mn}(\eta\text{-C}_5\text{H}_5)$	$\text{Cr}(\eta\text{-C}_6\text{H}_6)$	$\text{V}(\eta\text{-C}_7\text{H}_7)$	$\text{Ti}(\eta\text{-C}_8\text{H}_8)$
Optimal $\theta(^{\circ})$:	-26	-6	0	3	9	13

The driving force for distortion can be traced in each case to orbitals of e_1 symmetry, which are in phase combinations of the polyene e_1 orbitals with the metal xz , yz orbital set. The shape of one component of this

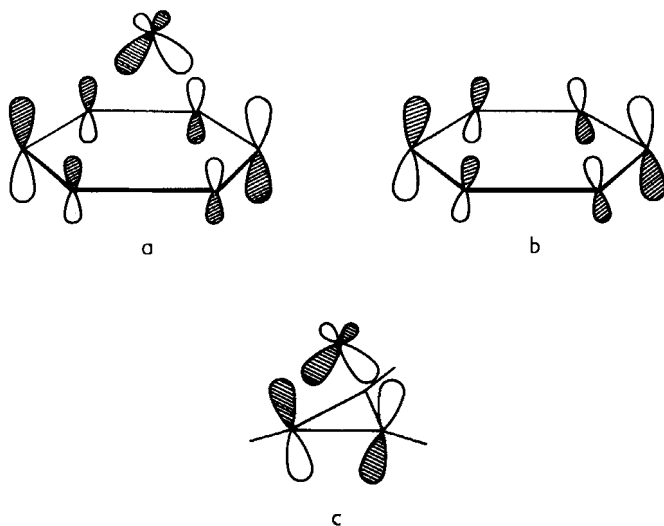


FIG. 20. (a) One component of the bonding e_1 metal-benzene molecular orbital set. Diagrams (b) and (c) illustrate the effect of tilting the p_π orbitals of the benzene and cyclopropenyl rings.

orbital for a planar benzene ring is illustrated in Fig. 20a. This orbital combination is stabilized for a distorted benzene geometry with the hydrogens bent toward the metal because the metal-carbon p_π overlaps are increased (77, 128). This argument is illustrated schematically in Fig. 20b. For smaller rings (e.g., cyclopropenyl), maximum overlap is achieved when the ligand π -set tilts outward as shown in Fig. 20c. Parenthetically it may be mentioned that the bending away of substituents on a complexed ethylene (see Section III,A) may be readily understood as a limiting case for the arguments cited above.

E. Bent Sandwich Complexes

Recently, elegant structural, photoelectron spectroscopy, and electron paramagnetic studies by M. L. H. Green (100), J. C. Green (98), Prout (97), and Dahl (177) have resulted in a detailed picture of the bonding in complexes $M(\eta\text{-C}_5\text{H}_5)L_n$ ($n = 1\text{--}3$). These experimental studies have substantiated the molecular orbital picture developed for these complexes by Fenske and Lichtenberger (178) and by Lauher and Hoffmann (134). There has been some disagreement in the past about the precise

nature of the hybrids used for bonding by the "bent" electron-deficient $M(\eta\text{-C}_5\text{H}_5)_2$ fragments (2, 12, 23), but these have been largely resolved by the recent theoretical and experimental studies noted above.

The way in which the d -type molecular orbitals of the $M(\eta\text{-C}_5\text{H}_5)_2$ fragment change as a function of the bending angle θ is illustrated in Fig. 21. Typically, the metals, M , have 4 or fewer d electrons and, therefore, it is the three lower-energy orbitals that play a primary role in coordinating the additional ligands, L . Contour plots of the relevant b_2 , $1a_1$, and $2a_1$ molecular orbitals derived from extended Hückel calculations (134) are shown in Fig. 22. The b_2 molecular orbital has chiefly d_{yz} character, and the two a_1 orbitals contain contributions from the metal s , p_z , $d_{x^2-y^2}$ and d_{z^2} orbitals. The $1a_1$ orbital is directed primarily along the y axis and may be described as essentially nonbonding. The $2a_1$ orbital is hybridized away from the C_5H_5^- ligands and is ideally placed to interact strongly with the donor orbitals of the incoming ligands. This strong interaction is an important feature of the molecular orbital correlation diagram for the $[M(\eta\text{-C}_5\text{H}_5)_2L_2]$ complex, which is illustrated in Fig. 23.

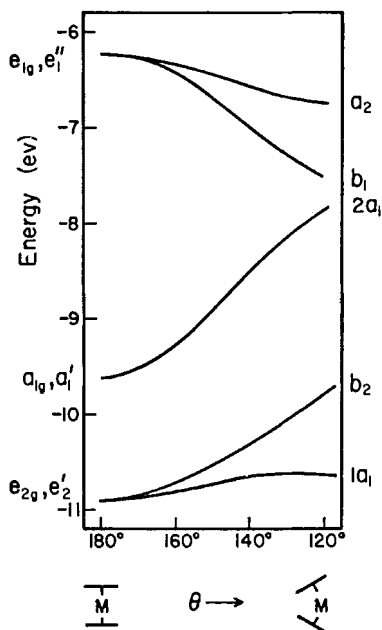


FIG. 21. Molecular orbitals of $M(\eta\text{-C}_5\text{H}_5)_2$ as a function of the bonding angle θ . [Reproduced from Lauher and Hoffmann (134), by permission of the American Chemical Society.]

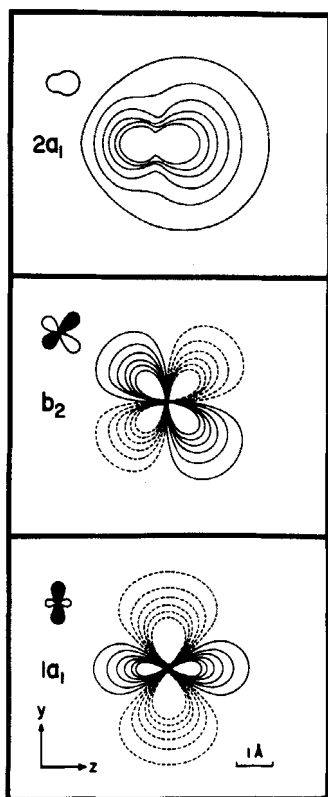


FIG. 22

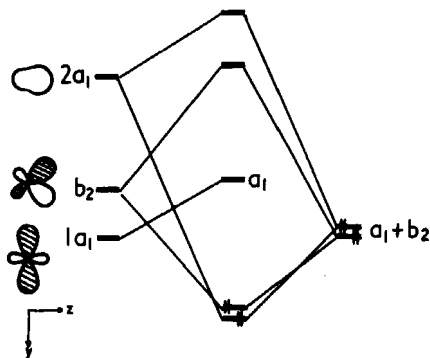


FIG. 23

FIG. 22. Electron density contour maps of the three frontier orbitals of electron-deficient $M(\eta\text{-C}_5\text{H}_5)_2$ fragments. The plots represent a section through the yz plane. [Reproduced from Lauher and Hoffmann (134), by permission of the American Chemical Society.]

FIG. 23. Interaction diagram for $M(\eta\text{-C}_5\text{H}_5)_2\text{L}_2$. [Reproduced from Lauher and Hoffmann (134), by permission of the American Chemical Society.]

Calculations on model $M(\eta\text{-C}_5\text{H}_5)_2\text{L}_2$ complexes have demonstrated that the energy and composition of the resulting a_1 nonbonding orbital are sensitive to the $\text{L}-\text{M}-\text{L}$ bond angle. These calculations reproduce the trend of decreasing bond angle with d -electron configuration established by crystallographic studies (97) and may be summarized as follows:

d -electron configuration:	d^0	d^1	d^2
$\text{L}-\text{M}-\text{L}$ ($^\circ$):	94-97	85-88	76-82

Lauher and Hoffmann (134) have also considered the bonding of the

$M(\eta\text{-C}_5\text{H}_5)_2$ fragment with π -acceptor and -donor ligands and have emphasized the orbital interactions with conformational consequences, e.g., for carbene and olefin ligands. They have also discussed insertion reactions of olefins and carbon monoxide coordinated to this metal fragment (134).

F. Metal-Metal Bonded and Cluster Compounds

Complexes containing metal-to-metal bonds have been studied intensively for the past 15 years (42, 53, 122, 130, 147), but quantitative and semiquantitative theories of the factors that determine the structures and properties of these interesting compounds are still at an early stage of their development. The very different radial characteristics of nd , $(n + 1)s$, and $(n + 1)p$ valence orbitals of the transition metals (e.g., Fig. 24) permit a wide spectrum of metal-metal interaction types; these range from the weak interactions that result in antiferromagnetic properties for dimeric copper complexes (109) to the strong multiple metal-metal bonds that are an important feature of the low valent chemistries of rhenium and molybdenum (54). The d orbitals of the transition elements are, in general, very much spatially contracted, and, therefore, it is only at very short metal-metal distances that d - d overlap integrals become significant. In addition, for metal atoms with approximately half-filled d shells, the metal-metal bonding interactions are synergic and become stronger as the metals come closer together. A metal-metal bond order of four was first proposed for the $\text{Re}_2\text{Cl}_8^{2-}$ ion on the basis of the very short metal-metal bond length of 2.24 Å (cf., 2.75 Å in the metal) and the eclipsed rotameric conformation. Similar geometries have since been reported for $[\text{Cr}_2(\text{CH}_3)_8]^{4-}$, $\text{Cr}_2(\text{allyl})_4$, and $[\text{Mo}_2(\text{allyl})_4]$ (54). Recent X_α calculations on $[\text{Mo}_2\text{Cl}_8]^{4-}$ (168) have confirmed the dominant role of the d -orbital interactions in these dimers and the essential features of the quadruple metal-metal bonding scheme first proposed by Cotton and Harris (56).

For transition metals with more complete d shells, the metal-metal d -orbital interactions become progressively more repulsive as the antibonding metal-metal molecular orbitals are occupied and the synergic bonding effects noted above are lost. Indeed, for a typical metal-metal bond distance of 2.60 to 2.70 Å for a first-row metal at the right-hand side of the transition series, the d - d overlap integrals are almost insignificant and the bonding situation tends to be dominated by the metal s and p orbitals that overlap very effectively at these bond lengths (155). The contribution made by the s and p orbitals are also sensitive to

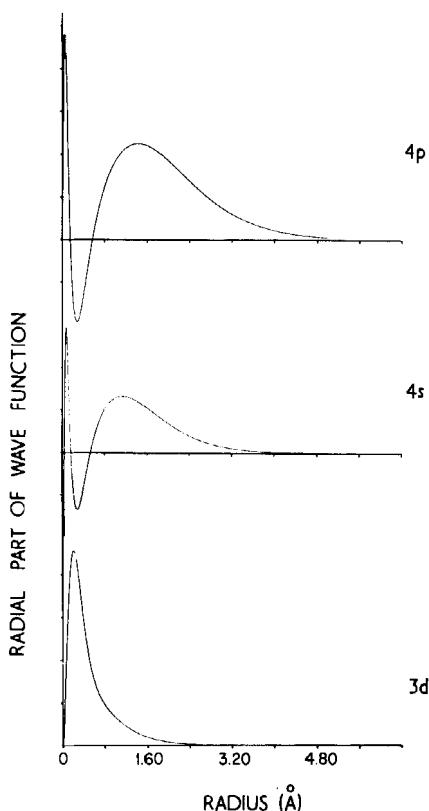


FIG. 24. Plots of the radial parts of the wave functions for cobalt 3d, 4s, and 4p orbitals.

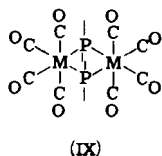
the $nd \rightarrow (n+1)s$ and $nd \rightarrow (n+1)p$ promotion energies, which, in turn, depend on the oxidation state of the metal and electron-donating or -withdrawing properties of the ligands bonded to the metal. Moreover, the electronic characteristics of these ligands can influence the relative proportions of metal d , s , and p character in those molecular orbitals that are metal-metal bonding and so affect markedly the strength and length of the metal-metal bonds. Indeed, bond length variations of up to 0.3 \AA have been reported for similar complexes that have identical formal bond orders (146). Elian *et al.* (77) have discussed how substitution of three terminally bound carbonyl ligands in a cluster by a benzene or cyclopentadienyl ligand can affect the lengths of the metal-metal bonds by altering the hybridization of the metal orbitals. Similar studies

on the effect of phosphine and halide substitution would be most interesting.

1. Dimeric Complexes

Several research groups have concluded on the basis of molecular orbital calculations that the metal-metal bonding is weak in the unbridged $[M_2(CO)_{10}]$ ($M = Mn, Te, \text{ or } Re$) dimers. A consequence of this weak interaction is the presence of a low-lying empty σ^* metal-metal antibonding orbital, and Gray and Levenson (135) have discussed the photochemical implications of this result. The displacement of the carbonyl ligands in the equatorial planes of the $[Mn_2(CO)_{10}]$ molecule toward the other metal atom has received several molecular orbital explanations. Brown and co-workers (27) have proposed that this distortion arises from an interaction of the carbonyl π^* -orbitals with the filled d orbitals on the nonadjacent metal atom. Elian and Hoffmann (78) have rationalized the effect on the basis of the different bonding capabilities of the axial carbonyl ligand and the metal trans to it. Other explanations based on interligand repulsion effects have also been proposed (32).

In bridged metal-metal bonded dimeric complexes, the relative importance of metal-metal and bridging ligand effects are more difficult to unravel. Dahl and his co-workers have elegantly exploited systematic crystallographic analyses to detail the stereochemical consequences of valence-electron addition or removal in dimeric metal complexes (46, 47, 65, 230) and clusters (66, 88, 204, 205, 213, 216, 222). Their experimental work has been neatly underpinned by nonparameterized approximate Hartree-Fock molecular orbital calculations (217) on the phosphido-bridged dimers $[Cr_2(CO)_8(\mu-PR_2)_2]^{n-2}$ and $[Mn_2(CO)_8(\mu-PR_2)_2]^n$ ($n = 0, +1, \text{ or } +2$):



The crucial molecular orbital in these molecules appears to be one of B_{3u} symmetry, which is an in-plane σ^* -orbital and is strongly antibonding between the metals. The electron population of this orbital is $(B_{3u})^2$, $(B_{3u})^1$, and $(B_{3u})^0$ when n is 0, +1, and +2, respectively, in the complexes above. Removal of electrons from this antibonding orbital

accounts for the metal-metal bond-shortening effects and bond angle changes at the bridging ligand atom, as established by crystallographic studies on these and related molecules.

2. Cluster Compounds

The geometries of metal carbonyl and metallocarborane cluster compounds have been systematized recently by a set of simple rules described collectively as the *polyhedral skeletal electron pair theory* (153, 218, 232). This approach originated from a perceptive analogy between isostructural metal carbonyl and borane polyhedral cluster molecules (232), and its applications have been widely discussed and reviewed (147, 153, 210, 218, 233, 234, 235, 240). In this review,

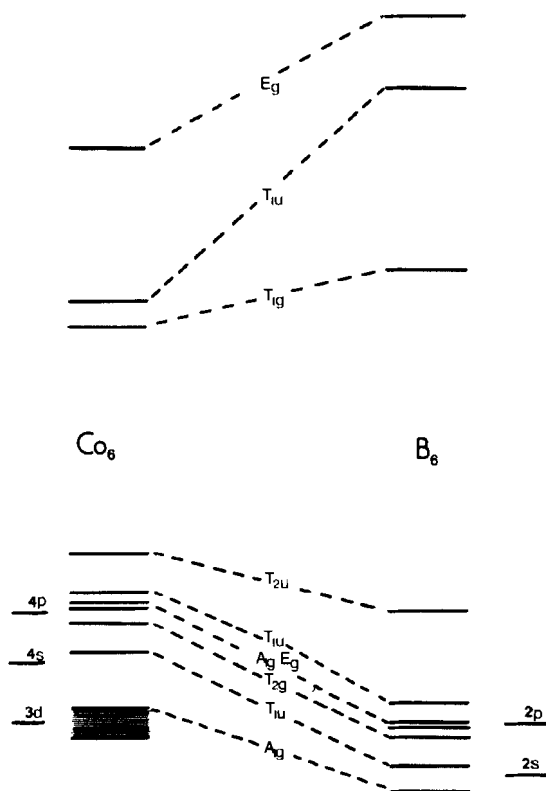


FIG. 25. Molecular orbitals for octahedral B_6 and Co_6 clusters based on extended Hückel calculations (155).

therefore, only the theoretical basis for this important generalization will be discussed.

As noted above, the metal-metal d overlaps, because metal-metal distances characteristic of metal carbonyl cluster compounds are small and, therefore, when metal atoms aggregate to form a cluster these atomic orbitals interact only weakly and generate a narrow band of molecular orbitals. By contrast, the large overlap integrals that result from the overlap of the more diffuse s and p valence orbitals give rise to a wider spectrum of molecular orbital energies (155). Furthermore, as the individual overlap terms are comparable to those for boron atoms in a similar situation the pattern of molecular orbitals generated bears a striking resemblance to that reported for isostructural boron polyhedra (139) (e.g., Fig. 25). Similar molecular orbital correlation diagrams are observed for the other platinum metals. For gold clusters, different molecular orbital patterns are generated, however, because the metal-metal p_π - p_π orbitals overlaps are very small (159).

The axially symmetric metal carbonyl fragments $M(\text{CO})_n$ ($n = 1, 3, 4$) have three outpointing hybrid orbitals with a high proportion of s and p orbital character, which are suitable for forming cluster skeletal molecular orbitals (77, 78, 238). The number and radial characteristics of these frontier molecular orbitals, which are illustrated schematically in Fig. 26a, are reminiscent of the frontier orbitals of a main group diatomic hydride fragment $E-H$, where $E = \text{C}$ or B (Fig. 26b). To describe this similarity the term *isolobal* has been introduced (77). Molecular orbital

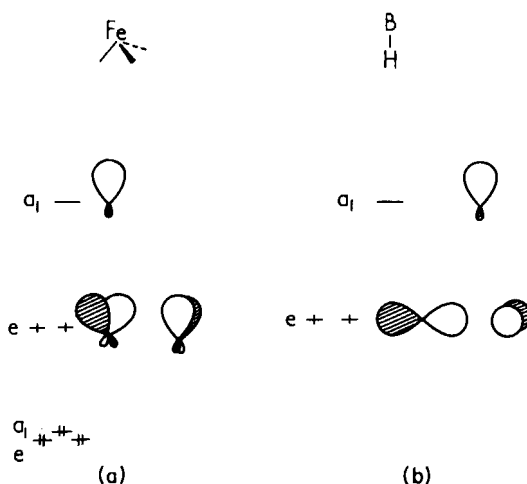
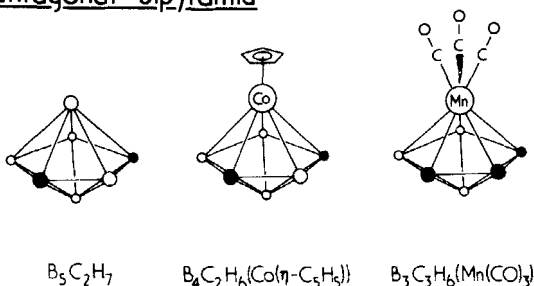
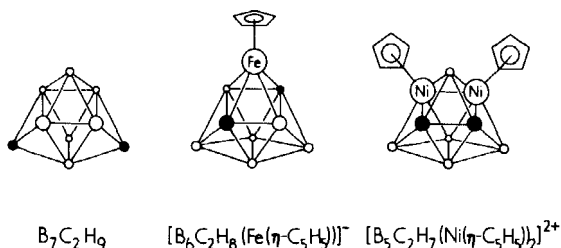


FIG. 26. Frontier molecular orbitals of isolobal (a) $\text{Fe}(\text{CO})_5$ and (b) BH fragments (78).

Pentagonal bipyramid

8 Skeletal Electron Pairs

Tricapped Trigonal Prism

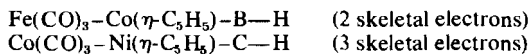
10 Skeletal Electron Pairs

○ = B-H

● = C-H

FIG. 27. Examples of isostructural carboranes and metallocarboranes that are skeletally isoelectronic (235).

studies have shown that these axially symmetric $M(CO)_n$ fragments also have $(6 - n)$ nonbonding molecular orbitals with a high proportion of d -orbital character (77, 78, 238). Thus, the frontier orbitals of the $M(CO)_n$ fragments are occupied by $[x - 2(6 - n)]$ electrons, where x = the number of valence electrons associated with the metal. The following fragments, as a consequence, are both *isolobal* and pseudo isoelectronic:



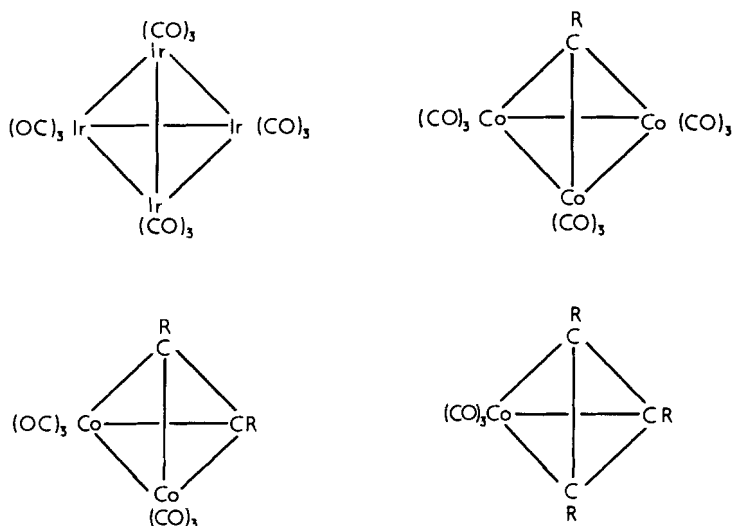


FIG. 28. Substitution of isolobal and isoelectronic CH and $M(CO)_3$ ($M = Co$ or Ir) fragments in tetrahedral clusters. It is interesting that the final member of the series C_4H_4 (tetrahedrane) has not been isolated.

and are structurally interchangeable. Two series of isostructural metallo-carboranes and metallocarbanes illustrating this structural substitution principle are shown in Figs. 27 and 28. In addition, the results of molecular orbital calculations reported for polyhedral borane anions and hydrocarbons can be used to estimate the stable closed-shell electronic requirement for metal carbonyl cluster compounds. This approach has been successfully used to account for the polyhedral geometries of the osmium cluster compounds shown in Figs. 29 and 30 (218).

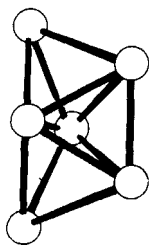


FIG. 29

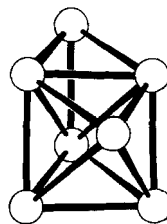
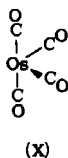


FIG. 30

FIG. 29. The bicapped tetrahedral geometry established for the $Os_6(CO)_{18}$ metal cluster. For reasons of clarity the carbonyl ligands have been omitted from the illustration.

FIG. 30. The capped octahedral geometry established for the $Os_7(CO)_{18}$ cluster. For reasons of clarity the carbonyls have been omitted.

When the metal carbonyl fragment departs from axial symmetry, the isolobal analogy is no longer strictly valid and the number of valence orbitals and electrons contributed by the metal for skeletal bonding depends on the precise metal ligand geometry. For those fragments with geometries related to the octahedral parent, the nonbonding t_{2g} set (stabilized somewhat by interaction with the carbonyl π^* -orbitals) is "remembered." These fragments have $6 - n$ frontier orbitals suitable for forming skeletal molecular orbitals and $(x - 6)$ electrons occupying them (78). For example, the C_{2v} $\text{Os}(\text{CO})_4$ fragment (X) has 2 valence electrons occupying the frontier orbitals shown in Fig. 31. These orbitals bear a striking resemblance to the frontier orbitals of methylene (CH_2), and the molecular orbitals pattern of $\text{Os}_3(\text{CO})_{12}$ (132) resembles closely that of cyclopropane.



The role of bridging groups in metal carbonyl cluster compounds is still not completely understood but has been discussed qualitatively by

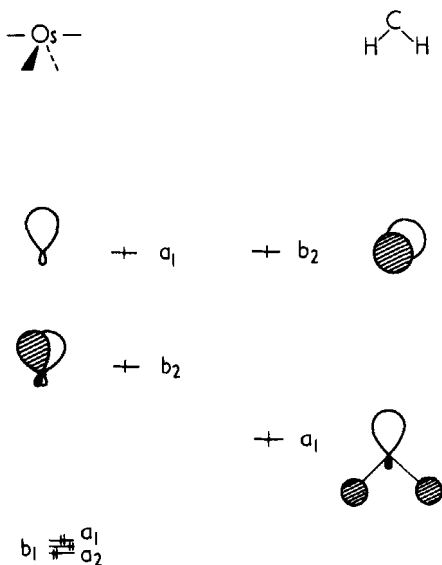


FIG. 31. Frontier molecular orbitals of isolobal (C_{2v}) $\text{M}(\text{CO})_4$ and CH_2 fragments.

several researchers (22, 129, 146, 155). Dahl and his co-workers (216, 222) have studied in some detail the electronic and structural properties of triangular and tetrahedral metal cluster complexes with chalcogenide and pnictogenide bridging ligands. Research in this area has recently received an additional impetus with the discovery that the Fe_4S_4 cluster moiety is an important feature of the bacterial redox proteins known as the ferredoxins (203).

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Metal Atom Synthesis of Organometallic Compounds

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I

INTRODUCTION

The first report of the preparation of organometallic compounds by direct reaction between metals atoms and organic ligands came in 1969 (127). Research into synthesis using metal atoms has expanded steadily since then and now seems likely to increase very rapidly as the necessary equipment becomes commercially available.¹ The field has been reviewed in part before (55, 67, 78a, 84a, 129), but no comprehensive review of the organometallic aspects has yet been published.

In this chapter we consider the formation of organometallic compounds from metal atoms in two ways. In the text, the reactions of broad classes of compounds with metal atoms are discussed, and in the

¹ Apparatuses are marketed by G. V. Planer of Sunbury, England, and by Kontes of Vineland, New Jersey.

Appendix, we present tables summarizing the reactions that have been carried out with each metal vapor. For the sake of completeness, we have included a few types of reactions in which the products are not organometallic e.g., the formation of metal-phosphine and metal-acetyl-acetone complexes. Our review covers the literature up to February 1976 with selected references added in proof in December 1976.

A. *Fundamentals of Metal Atom Synthesis*

Metal atoms can be formed by thermally vaporizing metals under vacuum. The required temperatures range from 200° (mercury) to 3000°C (tungsten). Most transition metals give monatomic vapors, but dimers and polymers form a small fraction of the vapors of many of the Main Group metals. The heats of formation of gaseous metal atoms are high: among the transition metals values range from 281 kJ/mole⁻¹ for manganese to 837 kJ/mole⁻¹ for tungsten. The enhanced reactivity of metal atoms compared with bulk metals is due partly to the endothermicity of the atoms and partly to kinetic factors.

The technique that has been generally adopted for reacting thermally generated metal atoms with organic compounds, can be summarized as follows. (a) The metal is vaporized at a controlled rate (typically in the range 0.2–2.0 gm hour⁻¹) by heating under high vacuum (<10⁻³ torr). (b) The atoms are allowed to pass by a line-of-sight path to the cooled walls of the vacuum chamber where they are condensed *either* with excess of the vapor of an organic compound *or* into a solution of the compound in an inert solvent. The walls of the vacuum chamber must be cold enough to keep the vapor pressure of any of the components in the system below 10⁻³ torr. This usually requires a temperature below -100°C, and liquid nitrogen cooling is used most commonly. (c) Products are separated from excess reactants by standard organometallic techniques.

Low-temperature reactions of metal atoms have also been studied extensively by vibrational and electronic spectra. In most studies, a noble gas has been used as a diluent for a mixture of metal atoms and compound condensed on a window cooled to 20 K or lower. This permits controlled diffusion of reacting species and gives high quality spectra of reaction products (90). Alternatively, metal atoms can be condensed with the vapor of a pure ligand on a cooled window. This technique works best when the ligand can be subsequently pumped away to leave a thin film of an organometallic compound, the spectra of which can be measured.

When metal atoms and organic compounds are condensed on a cold

surface, polymerization of the metal atoms to form solid metal will always be the kinetically and thermodynamically most favored reaction. The desired atom-molecule reaction will only compete if there is a large excess of the organic molecules; atom-molecule ratios of 1:10 to 1:50 are commonly used to obtain acceptable yields of organometallic products based on the metal vapor condensed. If a low ratio of metal atoms to compound is used, the reaction product may be destroyed by reacting with metal atoms, and both the reaction products and any excess reactants are likely to be strongly adsorbed on aggregates of metal atoms. As a consequence, reaction with metal atoms is not a satisfactory method for converting more than a small portion of a sample of an organic compound into an organometallic compound. Yields in metal atom reactions are usually quoted as the percentage of the metal vaporized appearing in the final product, with the assumption that a large excess of the organic reactant has been present.

Simple alkanes are generally unreactive toward metal atoms at low temperature. This is a great convenience in metal atom synthesis as alkanes can be used as diluents or solvents for ligands. Thus, methylcyclohexane has been used most commonly as solvent when reacting metal atoms with solutions of ligands. Under some conditions, it may be possible to abstract hydrogen atoms from tertiary carbon atoms and other acidic centers in alkanes; for example, $\text{HCo}(\text{C}_4\text{H}_9)_2$ is reported to be one of the products from the reaction of cobalt atoms with a 1:1 mixture of C_4H_{10} and Me_3CH (104, 110).

B. Experimental Methods

It is not a purpose of this chapter to consider experimental techniques in atom chemistry in detail. The different forms of apparatus and experimental techniques which have been used, have been thoroughly reviewed previously (55, 67, 129, 131a).

All the methods used to evaporate metals for atom synthesis were developed originally for the deposition of thin metal films. The more important of these techniques are shown schematically in Fig. 1a-d. Most of the evaporation devices can be scaled to give amounts of metal ranging from a few milligrams per hour for spectroscopic studies to 1-50 gm/hour for preparative synthetic purposes. Evaporation of metals from heated crucibles, boats, or wires (Fig. 1a-c) generally gives metal atoms in their ground electronic state. Electronic excitation of atoms is possible when metals are vaporized from arcs, by electron bombardment, or with a laser beam (Fig. 1d). The lifetime of the excited states of

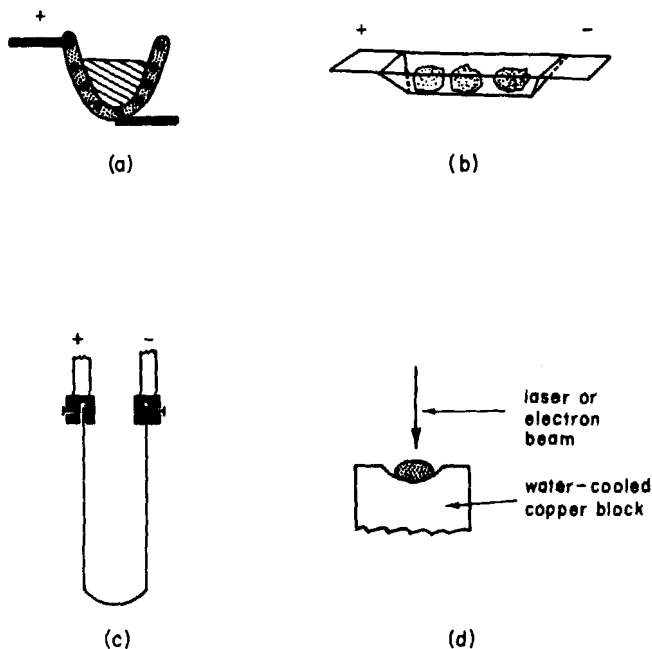


FIG. 1. Methods for forming metal vapors. (a) Evaporation from a resistance-heated, alumina-coated Mo or W spiral. This is a method suitable for Cr, Mn, Fe, Co, Ni, Cu, Pd, Ag, Au and other metals that do not attack alumina. (b) Evaporation from a resistance-heated Ta or W boat. This method is useful for V, Cr, and some lanthanides. (c) Sublimation from a resistance-heated free-hanging loop of wire, e.g., Ti, Mo, or W. (d) Evaporation from a cooled hearth using laser or electron bombardment heating. This method may be used with all metals.

transition metal atoms is usually so short that excited states will have decayed to the ground state before the atoms react on the walls of the vacuum chamber. Some excited states of Main Group metals are much longer lived and will be condensed on the cold surface where they may exhibit chemical properties different from those of ground-state atoms (110).

At present two main types of apparatus are in use for preparative-scale, metal atom chemistry.

1. A static glass or metal vacuum chamber with cooled walls, housing a metal evaporator and a system for distributing the vapor of compounds to be condensed with the metal atoms onto the cold walls (Fig. 2). The system for distributing vapor can be quite crude and yet effective because of the rapid expansion of vapors under the high vacuum in the

reaction vessel. At the end of cocondensation, the reaction vessel is either warmed up to a temperature that permits isolation of the product by vacuum line or Schlenk-type techniques, or another reagent is condensed into the vessel to react with the product *in situ*. The latter method is particularly useful if the product is thermally very unstable. Those products, that cannot be pumped or dissolved out of the reaction vessel may have to be scraped off the walls. Inert atmospheres must be maintained in all product recovery operations because, even if the product is not air-sensitive, finely divided metal residues in the vessel react very vigorously with air.

The scale of experiment that can be attempted in a static reactor is limited by heat conduction through the layer of condensate. Eventually, the condensate surface temperature is too high to allow further condensation; how quickly this point is reached depends on the rate of deposition of vapors and the amount of radiant heat from the furnace assembly.

2. A rotating, evacuated, cooled flask containing a metal evaporator (Fig. 3). Metal atoms can either be condensed with vapors or condensed

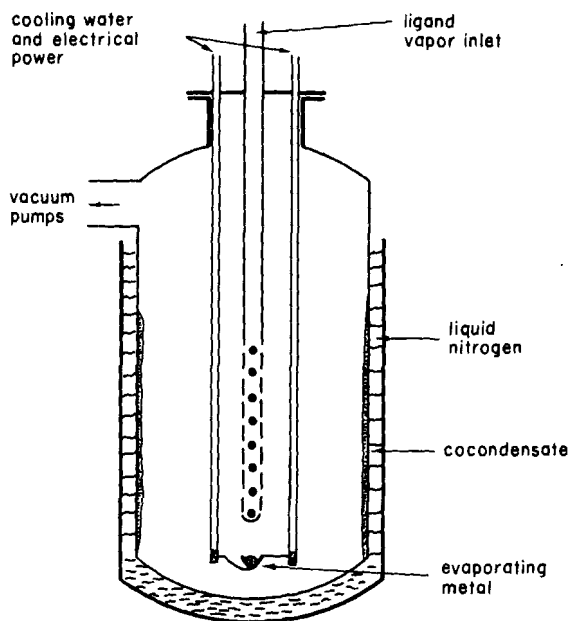


FIG. 2. Apparatus for cocondensing a metal vapor and the vapor of a compound on a gram scale.

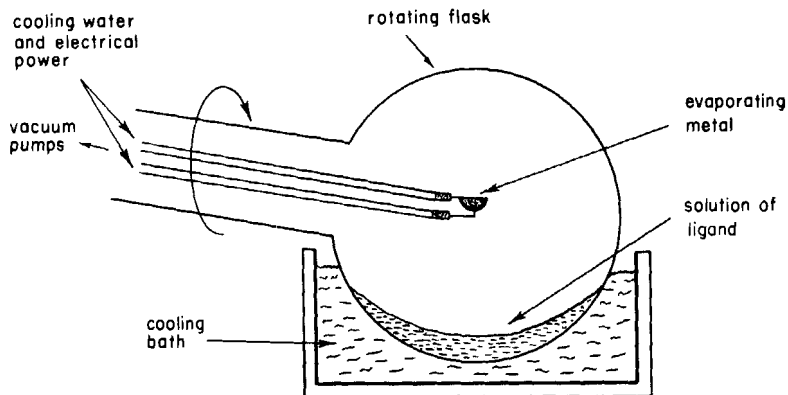


FIG. 3. Apparatus for condensing a metal vapor into a cooled solution of a compound.

into a solution of a compound that is carried over in a thin film as the flask rotates. The rotating flask offers most advantages over static reaction vessels when it is used as a solution reactor. The compound to be reacted with the metal vapor is dissolved to give a 10–20% solution in a solvent that is inert to the metal atoms and that has a low vapor pressure ($<10^{-4}$ torr) at its melting point. Products are either in suspension or in solution at the end of the experiment and can be recovered by standard anaerobic techniques. The method appears to give better yields than cocondensation when unstable complexes are being prepared, perhaps because the effective excess of the compound reacting with each metal atom is greater in solution than that easily obtained by cocondensation.

The type of apparatus used for spectroscopic studies of metal atoms is shown schematically in Fig. 4. For matrix isolation studies, the window

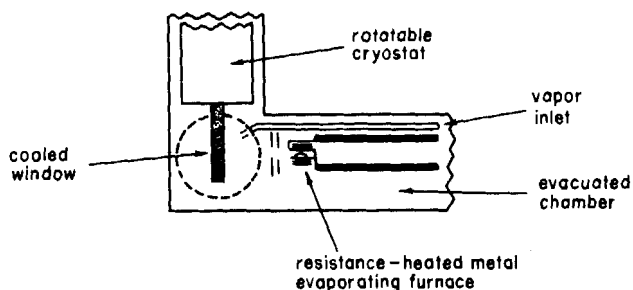


FIG. 4. Apparatus for spectroscopic studies of metal-atom reactions.

on which metal atoms, a compound, and a large excess of noble gas are to be condensed is normally cooled below 20 K. For thin-film studies, liquid nitrogen cooling may be sufficient to permit efficient condensation of the metal atoms and a reactant compound on the window; in these cases the metal-to-ligand ratio typically ranges from 1:20 to 1:50.

II

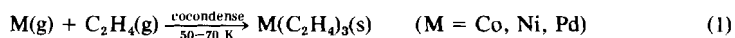
METAL ATOMS AND TWO-ELECTRON DONORS

A. Monoalkenes

The interaction of metal atoms with monoalkenes has been investigated on both a spectroscopic and preparative scale. It appears that the primary interaction between a metal atom and an alkene at low temperature is the formation of a π -complex. This may subsequently lead to a thermally stable π -alkene complex or to rearrangement products by hydrogen abstraction or reaction with another alkene moiety, depending on the electronic requirements of the metal and the particular alkene considered.

1. Ethylene

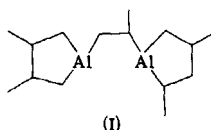
The formation of an initial π -complex between C_2H_4 and metal atom has been established at low temperatures (10 K) in a neon matrix by recent ESR studies for Ag, Al, Cu, Ga, and In (51, 52). An infrared study has shown that ethylene adds stepwise to nickel atoms in noble gas matrices giving NiC_2H_4 , $Ni(C_2H_4)_2$, and $Ni(C_2H_4)_3$ (48a). Products of type MC_2H_4 or $M(C_2H_4)_2$ are probably not stable outside the matrix. However, transition metals, such as, Co, Ni, and Pd, react with a large excess of C_2H_4 at 50 to 77 K to afford molecular complexes,



which are capable of discrete existence in the absence of free ligand (5a). Direct condensation of the metal vapor with C_2H_4 at -196°C affords $M(C_2H_4)_3$ in millimolar quantities and good yields. Although isolation of pure materials is hampered by the thermal instability of these complexes, it is relatively easy to examine their chemistry by subsequent reaction of the condensate at low temperature (50).

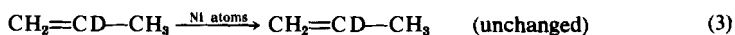
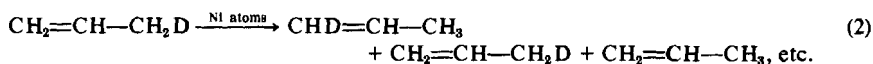
2. Propene, Butene, etc.

Skell has examined the interaction of a wide range of metal vapors (Al, Ni, Pd, Pt, Cr, Zr, Dy, Er and Co) with propene at -196°C by subsequent deuterolysis of the cocondensates. No complexes were isolated, but it was assumed that D_2O would label each metal-carbon bond present in the organometallic product. The deuterolysis of aluminum-propene cocondensates was extensively studied, the products being mainly d^2 -propane, various isomeric d^2 -hexanes as well as some d^0 - and d^1 -propene. The formation of this would be rationalized in terms of the intermediate formation of 1,2-dialuminoalkanes, aluminocyclopropanes, and aluminocyclopentanes (104, 110, 116), e.g.,

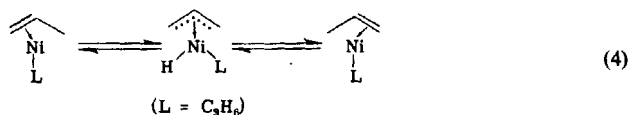


Similar results were obtained with erbium, dysprosium, and chromium vapors (104, 115). However, on deuterolysis, most transition metal cocondensates afforded mainly unlabeled propene with only two traces of propane and hexanes (104, 107, 110). The differing reactions of metal vapors with propene were interpreted in terms of a change in the σ - and π -bonding propensities of the metal in the initial (unisolated) organometallic product on progressing along a period in the periodic table (110).

The structure and properties of the initial nickel atom-propene complex has received detailed attention by Skell. The use of isotopically labeled propenes demonstrated that exchange occurs between the 1- and 3-positions but not between either the 1- and 2- or 2- and 3-positions (10):



Similarly, condensation of a mixture of C_3H_6 and C_3D_6 with nickel vapor resulted in isotopic scrambling. The intraligand isomerizations may be explained in terms of a 1,3-hydrogen shift via a η^3 -allyl nickel hydride complex in equilibrium with a π -propene complex, e.g.,

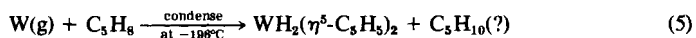


This reaction is consistent with 2 moles of propene being liberated on

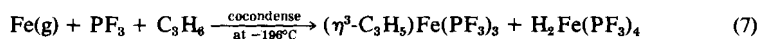
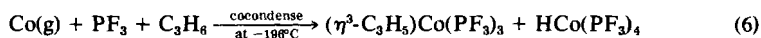
hydrolysis or upon treatment with butadiene (109), especially in view of the elegant demonstration of such an equilibrium in a related system ($L = PF_3$) by Bönnerman (11, 141).

Infrared studies of the direct interaction of cobalt, nickel, and palladium vapors with propene between 80 and 200 K indicate the presence of only a π -bonded alkene as was found in the reaction with C_2H_4 . Although the "allyl metal hydride" species was not observed, its presence, either in small concentration or as an intermediate in *subsequent* reactions, has been convincingly demonstrated by isotopic labeling in the case of nickel, and by trapping reactions in the case of iron and cobalt (see in following). The direct interaction of iron atoms with propene is different from those of cobalt, nickel, and palladium in that no π -alkene or π -allylic products are observed. Instead a product containing a free double bond is found (presumably a σ -allyl or σ -propenyl bond). As usual, manganese vapor was found to be unreactive (5a).

Butene and higher linear alkenes react with metal atoms in a similar manner to propene. In general, it is found that terminal alkenes are isomerized to nonterminal alkenes, presumably through the intermediacy of π -allyl metal hydrides by 1,3-hydrogen migrations (104, 110, 115). It is of interest that the nickel vapor-1-butene cocondensate will catalyze the isomerization of 1-butene to a mixture of *cis*- and *trans*-2-butenes at $-40^\circ C$, whereas the corresponding platinum-1-butene system will not (107, 109). Nevertheless, the labilizing effect of a metal atom on carbon-hydrogen bonds in alkenes appears to be a fairly general phenomenon, as is well demonstrated by the ability of tungsten atoms to react with cyclopentene to give a $\eta^5-C_5H_5$ complex (136):



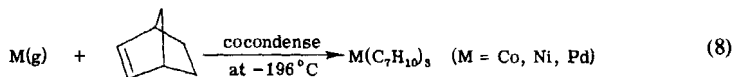
In contrast to C_2H_4 , the synthesis of simple substituted π -alkene-metal complexes from metal atoms is particularly difficult in view of the ease of hydrogen migration as well as the general destabilizing effect of an electron-donating group (i.e., $-CH_3$, etc.) on the metal-alkene bond (141). This instability may be put to synthetic advantage in the preparation of η^3 -allyl complexes (28, 134):



3. [2.2.1]-Bicyclohept-2-ene (Norbornene)

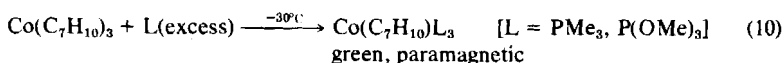
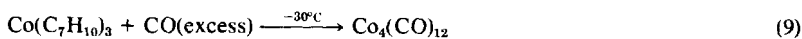
Metal-norbornene complexes are much more stable than the corresponding complexes with other disubstituted alkenes. This is due to the

relief of ring strain in the bicyclic system on coordination to a metal center. In addition, the inability of this ligand to form η^3 -allylic complexes makes it particularly attractive in metal atom syntheses. Condensation of either Ni or Pd vapors with an excess of norbornene at -196° affords relatively high yields ($\sim 50\%$) of stable complexes (134):



The high-temperature method represents a convenient one-step synthesis of these complexes in moderate (millimolar) quantities. There have been recent reports of multistep syntheses of both $Ni(C_7H_{10})_3$ and $Pd(C_7H_{10})_3$ by conventional reductive methods and their derivative chemistry has been extensively explored (35, 141).

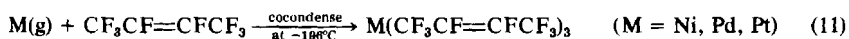
Cobalt vapor interacts with norbornene to produce $Co(C_7H_{10})_3$, a 15-electron complex, apparently isostructural with $Ni(C_7H_{10})_3$. The cobalt complex is soluble in hydrocarbon solvents to afford deep blue solutions decomposing rapidly and autocatalytically at -15° (5a, 134). It has not yet been possible to isolate this complex in a pure state but some of the reactions have been examined by trapping experiments:



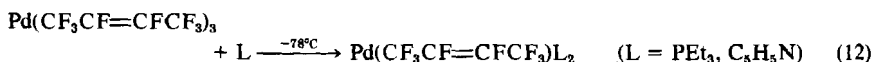
The interaction of norbornene with iron, chromium, molybdenum, and tungsten atoms affords highly unstable and uncharacterized systems of polymeric materials (102, 134). The use of other strained olefins, such as *trans*-cyclooctene, in metal atom syntheses has yet to be explored.

4. Haloalkenes

The interaction of metal atoms with carbon-halogen bonds is characterized by oxidative cleavage of that linkage and is discussed more fully in Section IV. An exception to this generalization appears to be perfluorobut-2-ene which reacts with transition metal atoms in a manner similar to C_2H_4 and norbornene (54, 55):



At least in the case of palladium the product is thermally unstable ($T_{dec} = -30^\circ\text{C}$), but it is a useful precursor in trapping reactions (54, 65):

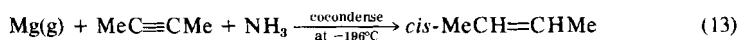


Complexation of Ni atoms to $\text{CF}_3\text{CF}=\text{CFCF}_3$ occurs in preference to the thermodynamically possible defluorination (see Sections IV and V). However, condensation of nickel vapor with C_2F_4 gives an explosive material; presumably defluorination is the dominant reaction in this case (132).

B. Alkynes

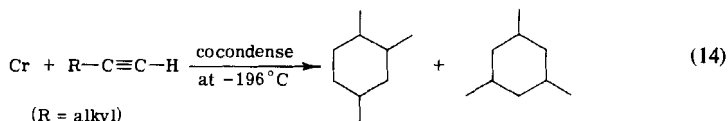
Alkynes have not yielded isolable organometallic complexes in their reactions with metal atoms, although the field has not been systematically examined.

Lithium atoms interact with C_2H_2 under matrix isolation conditions to afford LiC_2H_2 and $\text{Li}_2\text{C}_2\text{H}_2$ (39). In the presence of ammonia, magnesium atoms stereospecifically reduce alkynes, e.g.,



and, with silicon atoms, mostly polymers are obtained (104).

The vapors of the transition metals are effective in promoting the catalytic trimerization of alkynes, e.g.,



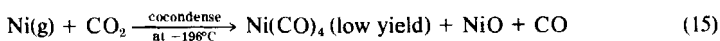
In no case has it been possible to isolate π -arene complexes from these reactions (109, 115).

C. Carbon Monoxide, Isocyanides, Phosphines, etc.

Reactions of metal atoms with CO have been studied extensively by matrix isolation spectroscopy, but little work has been done on making metal carbonyls from metal vapors on a preparative scale. Carbon monoxide has a high vapor pressure at liquid nitrogen temperature and cocondensation of the gas and metal vapors is possible only below 40 K, a temperature at which refrigeration costs are too high for preparative-scale work to be attractive. Nevertheless, the infrared and Raman spectra of metal carbonyls in inert gas matrices contain sharp, strong bands. With the aid of ^{13}C - or ^{18}O -labeled CO, the spectra often permit unambiguous assignments of the molecular formula and shape of a carbonyl to be made (84a).

Matrix isolation studies usually permit spectroscopic observation of the species $M(\text{CO})$, $M(\text{CO})_2$, . . . , $M(\text{CO})_n$, the coordinatively saturated molecule. In some early studies, species thought to be simple unsaturated carbonyls were in fact carbonyls of metal clusters $M_x(\text{CO})_y$; a very low concentration of metal in the matrix (e.g., 1 mol in 10^4 mol noble gas) has to be used to prevent clustering. All the partially coordinated carbonyls are only "matrix species," that is, they only exist when completely isolated from other molecules of their own kind or from CO. The coordinately saturated carbonyls are of more interest in the context of this review. The following new molecules have been reported: $\text{Au}(\text{CO})_2$ (84a); $\text{Ag}(\text{CO})_3$, $\text{Cu}_2(\text{CO})_6$ (46, 87); $\text{Pd}(\text{CO})_4$ (22), $\text{Pt}(\text{CO})_4$ (69); $\text{Rh}_2(\text{CO})_8$, $\text{Ir}_2(\text{CO})_8$ (37); $M(\text{CO})_6$ [$M = \text{Pr, Nd, Gd, Ho, Yb}$ (100), Ta (24), U (117)]. The Cu, Pd, Pt, Rh, and Ir carbonyls can be obtained by condensing the metal vapors with pure CO at 40 K and then pumping off excess CO to leave a film of the carbonyl. The Cu, Pd, and Pt carbonyls decompose under vacuum temperatures above -100°C , and the Rh and Ir carbonyls dimerize with loss of CO to give $M_4(\text{CO})_{12}$ above -60°C . The gold and silver carbonyls are not stable outside matrix isolation conditions. Unfortunately, the literature is presently unclear about the stability of the Ta and lanthanide hexacarbonyls outside a matrix.

Nickel atoms have been condensed with carbon dioxide,



However, there is no reaction between CO_2 and iron atoms (129). Nickel atoms also provide a route to both CS and CS_2 complexes: $\text{Ni}(\text{CS})_4$ (144), $\text{Ni}(\text{CS})_n$ ($n = 1-4$), and $\text{Ni}(\text{CS}_2)_x$ (91) have been reported. Only $\text{Ni}(\text{CS})_4$ appears to be stable outside matrix isolation conditions.

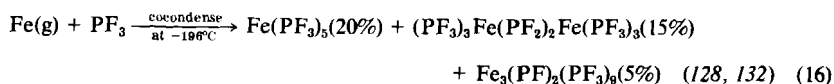
Carbonyls of some Main Group metals have been detected under matrix isolation conditions, e.g., $\text{Al}_x(\text{CO})_2$ (42), $\text{Ga}_x(\text{CO})_2$ (91), and $\text{Sn}(\text{CO})_n$ ($n = 1-3?$) (87). Bonding in these compounds is presumably of the "soft-acid-soft-base" class as in borane carbonyl, with only a minimal contribution from π -bonding.

A number of new metal-dinitrogen complexes of type $M(\text{N}_2)_n$ have been detected in the reaction of metal atoms with N_2 under matrix isolation conditions. Most strikingly, nickel atoms and nitrogen give $\text{Ni}(\text{N}_2)_4$ (45). However, this is strictly a "matrix species," and it decomposes on removal of the matrix gases even at very low temperatures. It appears to be stable up to -150°C isolated in an SF_6 matrix. Mixed CO/N_2 complexes have also been prepared in matrices but their stabilities outside the matrix are not reported (72).

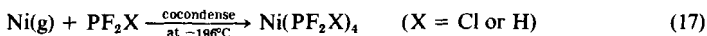
Condensation of metal atoms with nitric oxide may be accompanied

by oxidation of the metal. Thus, no $\text{Cr}(\text{NO})_4$ was isolated by condensing chromium vapor with NO at -196°C . Mixtures of PF_3 , NO, and BF_3 condensed with Mn, Fe, or Co yielded the mixed complexes $\text{Mn}(\text{NO})_3\text{PF}_3$, $\text{Fe}(\text{NO})_2(\text{PF}_3)$, and $\text{Co}(\text{NO})(\text{PF}_3)_3$ (84). The role of the BF_3 is not understood but in the absence of this gas the cocondensates exploded on warming from -196°C . Condensation of lithium atoms with NO in an argon matrix gives LiON (3), but there is little doubt that with transition metal atoms complexes formed are mainly of the type MNO . Nitric oxide has been less popular than CO and N_2 for matrix isolation studies of reactions with metal atoms because NO dimerizes to N_2O_2 which can itself coordinate to metals, making the spectroscopy of the system difficult to interpret.

Direct condensation of metal vapors with trifluorophosphine at -196°C provides a convenient alternative to the high-pressure route to metal- PF_3 complexes. The reactions of Mo, Cr, Co, Ni, and Pd vapors with PF_3 yield only one volatile product in each case, namely $\text{Mo}(\text{PF}_3)_6$ (132), $\text{Cr}(\text{PF}_3)_6$, $\text{Co}_2(\text{PF}_3)_8$, $\text{Ni}(\text{PF}_3)_4$, and $\text{Pd}(\text{PF}_3)_4$ (128), respectively. The yields are good, 40–100% depending on the metal vapor used. Some defluorination of the PF_3 accompanies the formation of $\text{Cr}(\text{PF}_3)_6$. No complex could be isolated from the manganese vapor- PF_3 reaction, although some defluorination seems to have occurred. The reaction of iron and PF_3 is complex,



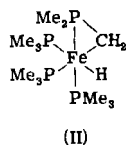
It is interesting that cobalt and PF_3 do not give $(\text{PF}_3)_3\text{Co}(\text{PF}_2)_2\text{Co}(\text{PF}_3)_3$, although this compound is a by-product of the high-pressure synthesis of $\text{Co}_2(\text{PF}_3)_8$ (67a). Nickel atoms react with difluorophosphines (94, 121), e.g.,



Trifluorophosphine is a very convenient ligand in metal atom chemistry to use along with other ligands, e.g., in the stabilization of metal arene complexes (Section III,B). Reaction of a mixture of PF_3 and PH_3 with nickel vapor yields $\text{Ni}(\text{PF}_3)_3\text{PH}_3$ and $\text{Ni}(\text{PF}_3)_2(\text{PH}_3)_2$ but no $\text{Ni}(\text{PH}_3)_4$. Attempts to make $\text{Ni}(\text{PH}_3)_4$ lead to hydrogen evolution from the ligand during or after condensation with the nickel vapor (128).

Trimethylphosphine condensed with cobalt nickel and palladium gives low yields of the known $\text{Co}(\text{PMe}_3)_4$, $\text{Ni}(\text{PMe}_3)_4$, and $\text{Pd}(\text{PMe}_3)_4$. The product from iron and trimethylphosphine is also formally $\text{Fe}(\text{PMe}_3)_4$ (134), but it is identical to the product obtained by Muetterties by

reduction of $(\text{Me}_3\text{P})_3\text{FeCl}_2$ and is best formulated (95) as



Initial attempts to form alkyl isocyanide complexes from metal atoms led to polymerization of the isocyanides (133). However, a recent report suggests that $\text{Ni}(\text{RNC})_4$, $\text{Fe}(\text{RNC})_5$, and $\text{Cr}(\text{RNC})_6$ can be made directly from the respective atoms and RNC at -196°C (98).

III

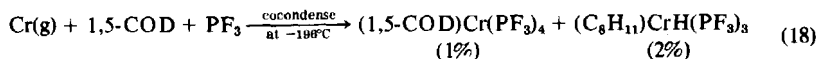
METAL ATOMS AND MANY-ELECTRON DONORS

A. Dialkenes

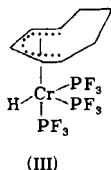
1. 1,3- and 1,5-Cyclooctadiene

The reaction of metal atoms with 1,5-cyclooctadiene (1,5-COD) offer special scope for forming new "naked metal" systems [Wilke (142)] i.e., complexes in which the ligands are readily displaced. The desire to explore these reactions was the impetus to developing the rotary solution reactor (81) which facilitates the reaction of metal atoms with slightly volatile or involatile ligands and, most important, aids the isolation of thermally unstable compounds ($T_{\text{dec}} \approx -60^\circ\text{C}$) in a pure state.

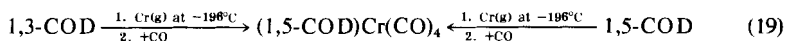
All of the reactions of 1,5-COD examined so far have been with transition metal atoms. With titanium, 1,5-COD affords a golden yellow condensate, decomposing at too low a temperature (ca. -110°C) to permit characterization. Similarly, chromium vapor interacts with solutions of 1,5-COD in methylcyclohexane giving ill-defined green products (82, 134). This is confirmed by a low-temperature infrared investigation of the chromium 1,5-COD interaction showing extensive rearrangement of the organic moiety on reaction (5a). However, if chromium vapor is condensed with a mixture of 1,5-COD and PF_3 , two stable organometallic products are obtained:



The similar reaction with 1,3-COD affords only $(C_8H_{11})CrH(PF_3)_3$. The molecular structure of this product has been shown by X-ray diffraction to be the η^5 -cyclooctadienyl complex (140):

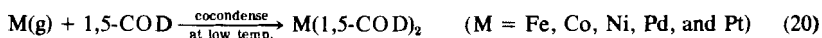


It is of interest that the same product is obtained from both 1,3-COD and 1,5-COD with chromium atoms and PF_3 , as this compound contains the proposed ring-intermediate for the often observed interconversion of coordinated 1,3- and 1,5-COD (23, 86). With CO both the chromium-1,3-COD and -1,5-COD condensates afford the same product,



presumably through an intermediate similar to that found with the PF_3 reaction (140). The corresponding reactions with molybdenum and tungsten atoms have not yet been examined in detail. However, preliminary infrared studies indicate that molybdenum vapor forms a complex with 1,5-COD that is stable below -35° and contains both mono- and bidentate 1,5-COD. At room temperature, this compound changes to a very air-sensitive material containing no free $C=C$ double bonds, but whose structure has not been fully determined (5a).

The reactions of the Group VIII elements with 1,5-COD have been examined in detail and in each case a similar product is obtained:



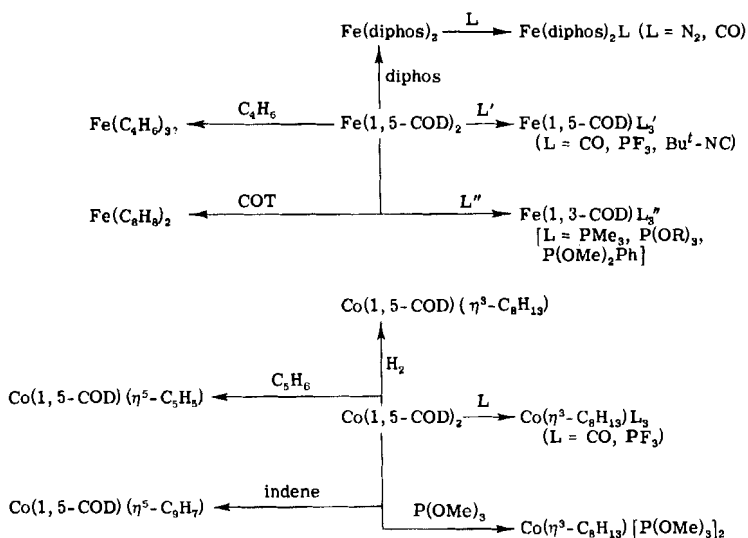
Infrared spectroscopic studies have been particularly useful in demonstrating the generality of this reaction. The spectra of the films of the complexes, obtained by depositing each of the metal vapors and excess 1,5-COD on a cold window and pumping off the excess ligand at $-70^\circ C$, are all extremely similar, i.e., the spectra of the new compounds of Fe, Co, and Pd are almost identical to the spectrum of $Ni(COD)_2$ with its known "tetrahedral" structure (25).

All known $M(COD)_2$ complexes can now be synthesized on a millimolar scale by the metal atom technique, although both $Ni(COD)_2$ and $Pt(COD)_2$ are more conveniently prepared by conventional synthetic routes (35, 99). The use of palladium vapor to afford $Pd(1,5\text{-COD})_2$ is a straightforward, high-yield ($>50\%$ *in situ*), one-step synthesis, offering advantages over the conventional method if isolation of a

metal-free material is not necessary. At present there is no conventional access to $\text{Fe}(\text{COD})_2$ or to $\text{Co}(\text{COD})_2$.

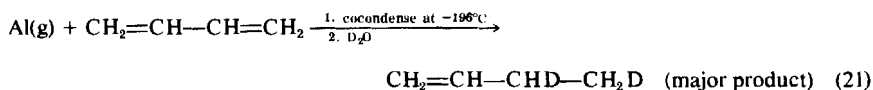
From the reaction of iron atoms with a solution of 1,5-COD in methylcyclohexane, brown crystals of $\text{Fe}(\text{1,5-COD})_2$ can be isolated in 40% yield (81). The thermal instability ($T_{\text{dec}} = -30^\circ\text{C}$) of this substance presents special problems in isolation of a pure product; however, subsequent reactions can often be performed on solutions freed from iron metal by low-temperature filtration. The yellow-brown cobalt system, $\text{Co}(\text{1,5-COD})_2$, may be prepared similarly (134).

A systematic examination of the stoichiometric and catalytic chemistry of both of these coordinatively unsaturated complexes is being undertaken. The following are some representative reactions (16, 81, 134):²

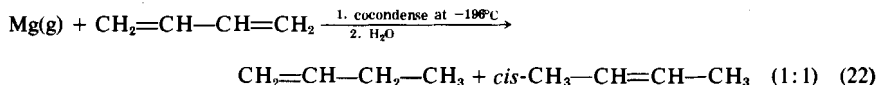


2. 1,3-Butadiene

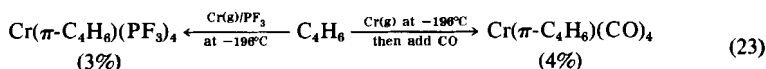
The 1,3-butadiene ligand rivals 1,5-COD and arenes in its utility in metal atom syntheses. Within the main group elements, hydrolysis of metal vapour-butadiene condensates indicate that σ -bonded complexes are generally produced (110, 116):



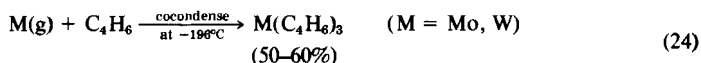
² COT = cyclooctatetraene.



Chromium atoms also react with butadiene to give a product that yields predominately *d*²-but-1-ene together with *cis*- and *trans-d*²-but-2-ene on deuterolysis. This can also be interpreted in terms of σ -bonded organo-metallic products. However, it is also possible to isolate a π -complex of butadiene by ligand stabilization of the low-temperature condensate (115, 138, 140):

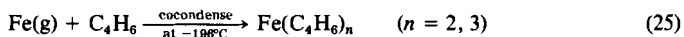


Unlike the chromium-butadiene reaction, the vapors of both molybdenum and tungsten afford thermally stable π -complexes that are air-stable, white crystalline solids (114):

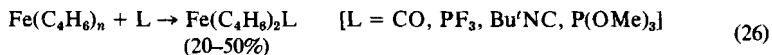


The molecular geometry of $\text{Mo}(\text{C}_4\text{H}_6)_3$, determined by X-ray crystallography, shows a trigonal prismatic coordination about the metal atom with each of the three equivalent C_4H_6 ligands in a cisoid configuration (110). No reports of the chemistry of these fascinating complexes has yet appeared.

Condensation of manganese and butadiene followed by addition of CO at -196°C gives a very low yield of $\text{Mn}(\text{C}_4\text{H}_6)_2\text{CO}$ (40). However, iron reacts quite efficiently and affords a red-brown complex that decomposes at about -5°C in the solid state:



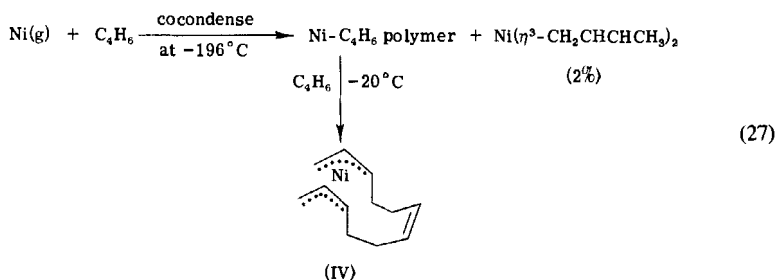
This system can also be synthesized by displacement of 1,5-COD from $\text{Fe}(\text{1,5-COD})_2$ with butadiene:



Although the complex has not been fully characterized, its use as an organometallic precursor is well-established.

Some of these derivatives are useful catalysts for the codimerization of dienes with acrylic esters (82, 138, 140, 143). The reaction between cobalt vapor and butadiene is complex, and the nature of the products remains to be elucidated. However, there is a report of the synthesis of the yellow complex $\text{HCo}(\text{C}_4\text{H}_6)_2$ from the condensation of a mixture of C_4H_6 and Me_3CH with cobalt vapor (104, 110).

The interaction of butadiene with nickel afford a gray, intractable, and nonvolatile material together with traces of a volatile yellow oil-containing bis(crotyl)nickel. Further reaction of the nonvolatile fraction with butadiene gives a bis(allyl)-C₁₂ nickel complex (IV) in good yield (109):

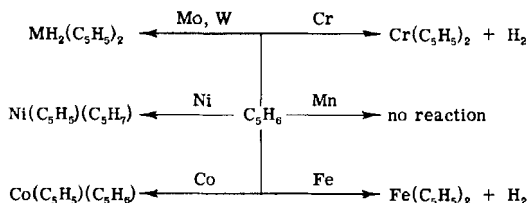


No organometallic products from the reaction of palladium or platinum vapors with butadiene have yet been reported. However, the platinum-butadiene condensate is a catalyst for the hydrogenation of butadiene, the product being mainly butane (104).

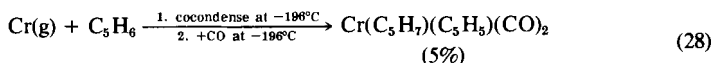
Catalytic oligomerization of butadiene is found to occur in most transition metal vapor-butadiene reactions. The organic products are COD, linear dimers and trimers, *trans, trans, trans*- or *cis, trans, trans*-cyclododecatriene or higher oligomers, the proportion of each depending on the metal used and the subsequent reaction conditions. In some cases, the organic product distribution can be greatly altered by cocondensation of catalysts such as Et₂AlCl, Al, and EtCl or phosphorus ligands (1, 2).

3. Cyclopentadiene

The interaction of metal atoms with cyclopentadiene is characterized by a tendency toward formation of a stable electronic configuration for the metal. Thus, cyclopentadiene undergoes the following reactions on condensation with metal vapors at -196°C (21, 115, 127, 136):

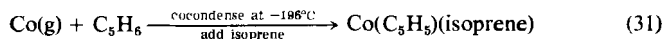
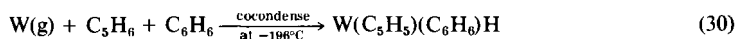
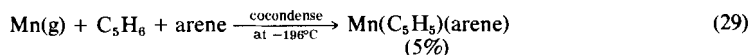


These reactions may proceed through an $M(C_5H_6)_2$ intermediate, but in the absence of isolated or trapped intermediates there is no compelling evidence that this is so. Chromium vapor- C_5H_6 condensates liberate H_2 only on warming, and, in this case, it has been possible to isolate a complex by trapping with carbon monoxide:

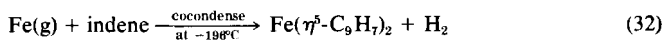


The reaction suggests that $Cr(C_5H_6)_2$ or more likely $CrH_2(C_5H_5)_2$ is present at low temperatures (50).

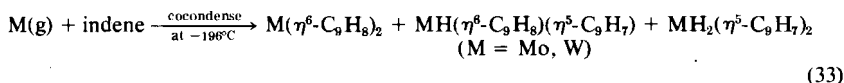
Although the foregoing reactions are quite facile, they are not competitive with the very well-established conventional methods for synthesis of metallocenes. Cyclopentadiene, nevertheless, can be a useful substrate in metal atom synthesis as part of a mixed-ligand system (6, 110, 136, 140), e.g.,



Related systems, such as indene and fluorene, often react in a manner similar to cyclopentadiene (38, 83):



In addition, these fused-ring systems allow a one-step syntheses of mixed arene-dienyl complexes (136):

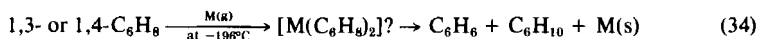


4. Other Dienes

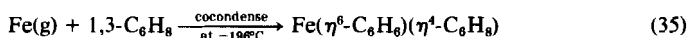
In view of the extensive chemistry evolving from the 1,5-COD-metal atom reactions, it is disappointing that norbornadiene does not undergo analogous reactions. Instead, the predominate products are usually dimers or polymers of norbornadiene; for example, with Ni vapor the *exo-trans-exo*-dimer is produced and Mo and W catalyze the polymerization of the free ligand by a ring-opening reaction (109, 110). Attempts at trapping products by addition of other ligands at low temperatures

have not yet been successful (134). The instability of the metal-norbornadiene interaction is presumably due to the smaller "bite" of chelating norbornadiene compared with the chelating 1,5-COD ligand. Relief of the considerable ring strain in norbornadiene is, therefore, best effected by polymerization rather than by complexation.

Both 1,3- and 1,4-cyclohexadienes undergo rapid and catalytic disproportionation in the presence of transition metal atoms, possibly through the intermediacy of a bis(diene)metal system



(although no such complex has yet been isolated). However, with iron vapor, it is possible to isolate a system conceivably derived from such a diene complex (143):



Other reactions of dienes with metal atoms are only of a limited synthetic use. Dibenzylideneacetone ($\text{PhCH=CH-CO-CH=CHPh}$; DBA) reacts with palladium vapor to afford $\text{Pd}_2(\text{DBA})_3$, a complex in which the coordination is through the two C=C units and does not involve the C=O (5, 92). Cobalt vapor undergoes an extremely complicated reaction with 1,4-pentadiene, producing pentenes, C_5H_8 , and various polymers as well as the organometallic product, $\text{HCo}(1,3\text{-pentadiene})_2$, which involves isomerization from a nonconjugated to a conjugated diene (104, 110).

B. Arenes

The synthetic potential of transition metal atoms in organometallic chemistry was first demonstrated by the formation of dibenzenechromium (127). Apart from chromium, Ti, V, Nb, Mo, W, Mn, and Fe atoms each form well-defined complexes with arenes on condensation at low temperatures. Interaction has also been observed between arenes and the vapors of Co, Ni, and some lanthanides. Most important, the synthesis of metal-arene complexes from metal vapors has been successful with a wide range of substituted benzenes, providing routes to many compounds inaccessible by conventional reductive preparations of metal-arene compounds.

1. Benzene and Alkyl-Substituted Benzenes

The only route to dibenzenetitanium so far described is the reaction of titanium atoms with benzene; the reductive routes that give access to arene complexes of Group V and VI metals fail for titanium. Although yields of about 30% are reported for the preparation of dibenzene-, ditoluene-, and dimesitylenetitanium, the reactions are more sensitive than most to the effect of excess metal. Unless the ligand-to-titanium ratio is high and the rate of deposition of titanium vapor kept low, the products seem to be catalytically decomposed by finely divided Ti metal (4a, 7).

Vanadium vapor has been used to prepare dibenzenevanadium (59), and it is expected that alkylbenzenes would also react smoothly with the vapor. A matrix isolation infrared study in which sputtered niobium atoms were reacted with benzene in an argon matrix at 30 K has given evidence for the formation of dibenzeneniobium (36).

Pure bis(alkylbenzene)chromium complexes are best prepared by the chromium vapor route as there is no rearrangement of the alkylbenzene that often accompanies the Fischer synthesis for these compounds. However, the yield of bis(alkylbenzene)chromium compounds are not high, rarely more than 20%; polymeric materials accompany the desired product (32, 83, 84).

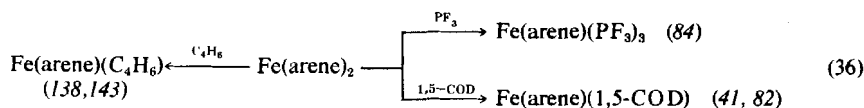
Molybdenum and tungsten atoms seem to react with alkylbenzenes more efficiently than chromium atoms; yields of 30 to 50% are reported (113). Conventional routes to the synthesis of tungsten-arene complexes are difficult and inefficient so that the ability to prepare these compounds in high yield via tungsten atoms is of special significance. Unfortunately, tungsten has a very high vaporization temperature and the scale of work with its vapor is necessarily limited.

By condensing chromium atoms, PF_3 , and arenes, numerous complexes of type $\text{Cr}(\text{arene})(\text{PF}_3)_3$ have been made. Such complexes may be formed even when the corresponding bisarenechromium cannot be prepared from chromium vapor (see following sections for examples).

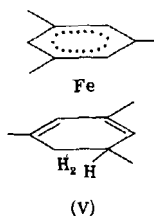
Diarenemanganese cations have not been formed by the metal atom route, but condensation of arenes, cyclopentadiene, and manganese gives low yields of $(\text{arene})\text{Mn}(\text{C}_5\text{H}_5)$. As cyclopentadiene does not react with manganese atoms, a primary manganese-arene reaction is postulated (131, 140) (see Section III,A,3).

As yet 20-electron diareneiron compounds have not been isolated as pure crystalline solids from iron vapor-arene reactions. However, infrared studies show that dibenzene-, ditoluene-, and dimesityleneiron are formed at low temperatures and decompose below -40°C (76). The

arene ligands are readily displaced from these complexes to form 18-electron compounds, e.g.,



Condensates containing dibenzeneiron or ditolueneiron decompose liberating the arene and iron metal, but dimesityleneiron decomposes to



in moderate yield (82).

Reactions of cobalt and nickel atoms with toluene and other arenes yield condensates in which the metal is in a very reactive state (105). However, none of the products of reaction of these condensates with other ligands has contained the arene coordinated to the metal. It seems possible that the condensates contain ditoluenecobalt and ditoluene-nickel, but in these complexes (unlike the chromium or iron complexes) the two arene rings are probably not symmetrically bonded to the metals.

2. Benzenes with Electronegative Substituents

Metal atoms are powerful scavengers of electronegative elements. When arenes with electronegative substituents react with transition metal atoms, the substituent may be scavenged or the unchanged arene ligand coordinated to the metal. The latter process has been observed only with V, Cr, Mo, and W atoms, and the vapors of these metals may be used to form a wide range of otherwise inaccessible sandwich compounds. Even with these metals, no bis(arene)-metal complex has been made in which the arene contains more than two electronegative substituents, i.e., halogen atoms, $-\text{CF}_3$, $-\text{OMe}$, or $-\text{COOMe}$.

Vanadium or chromium vapors, condensed with the appropriate arenes, form $\text{M}(\text{C}_6\text{H}_5\text{Cl})_2$, $\text{M}(\text{C}_6\text{H}_5\text{F})_2$, $\text{M}(\text{C}_6\text{H}_4\text{F}_2)_2$, and $\text{M}(\text{C}_6\text{H}_5\text{CF}_3)_2$. Chromium forms $\text{Cr}[\text{C}_6\text{H}_4(\text{CF}_3)_2]_2$ and $\text{Cr}(\text{C}_6\text{H}_4\text{Cl}_2)_2$, but the corresponding vanadium compounds are not obtained from vanadium vapor.

Clearly, there is a delicate balance between metal-arene formation and dehalogenation of the arene. Among the aforementioned isolated compounds, those of chromium show greater resistance to air oxidation than those of vanadium; for example, $\text{Cr}[\text{C}_6\text{H}_4(\text{CF}_3)_2]_2$ is completely stable in air (32, 59, 79, 115).

In an experiment to test the relative complexing and defluorinating effect of chromium atoms on fluorobenzenes, an equimolar mixture of each of the compounds C_6H_6 , $\text{C}_6\text{H}_5\text{F}$, . . . , C_6F_6 was condensed with chromium atoms and an excess of PF_3 at -196° . Each of the arenes formed a complex $\text{Cr}(\text{arene})(\text{PF}_3)_3$, the yield being a maximum for 1,4-difluorobenzene and a minimum for hexafluorobenzene (83). It seems likely that the thermodynamic stability of $\text{Cr}(\text{C}_6\text{H}_4\text{F}_2)(\text{PF}_3)_3$ is lower than that of $\text{Cr}(\text{C}_6\text{H}_6)(\text{PF}_3)_3$ so the higher yields of the former in the atom reaction must be due to kinetic effects. Ligands other than PF_3 are also effective in stabilizing chromium fluoroarene complexes. Thus, $\text{Cr}(\text{C}_6\text{H}_6)(\text{C}_6\text{F}_6)$ can be made, but not $\text{Cr}(\text{C}_6\text{F}_6)_2$ (83, 84). Complex $\text{Cr}(\text{C}_6\text{H}_6)(\text{C}_6\text{F}_6)$ is not oxidized by air and is, thus, one of the easiest of the known diarenechromium compounds to handle. Unfortunately, it is only formed in fairly low yield ($<10\%$) in the cocondensation of Cr atoms with C_6F_6 and C_6H_6 . Compound $\text{Cr}(\text{C}_6\text{F}_5\text{H})(\text{C}_6\text{H}_6)$ has been prepared similarly in about 10% yield using $\text{C}_6\text{F}_5\text{H}$ in place of C_6F_6 . The fluorine atoms on the coordinated rings of all the fluoroarenechromium complexes are susceptible to nucleophilic attack. Thus, the fluorine atoms in $\text{Cr}(1,4\text{-F}_2\text{C}_6\text{H}_4)_2$ can be displaced by methoxide. However, more extensive substitution chemistry is possible with $\text{Cr}(\text{C}_6\text{F}_6)(\text{C}_6\text{H}_6)$ and $\text{Cr}(\text{C}_6\text{F}_5\text{H})(\text{C}_6\text{H}_6)$, as both the hydrogen atoms are acidic and the fluorine atoms are readily displaced by nucleophiles. Treatment of $\text{Cr}(\text{C}_6\text{F}_5\text{H})(\text{C}_6\text{H}_6)$ with Bu^tLi at -78° followed by Me_3SiCl yielded $\text{Cr}(\text{C}_6\text{F}_5\text{SiMe}_3)(\text{C}_6\text{H}_6)$ (123, 124).

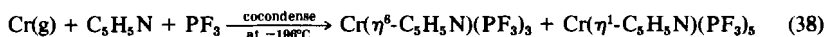
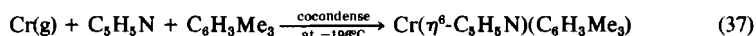
Methyl benzoate, anisole, and diphenyl ether each give sandwich compounds with chromium vapor, although in rather low yield (32, 55, 110). Chromium appears to attack alkyl ethers and this deoxygenation probably competes with complexation with the aromatic oxygen compounds. No simple product has been isolated from chromium atoms and aniline, but bis(*N,N*-dimethylaniline)chromium has been prepared (32). The behavior of molybdenum and tungsten vapors closely resembles that of chromium in reactions with oxygen- and nitrogen-substituted arenes (113).

Manganese, iron, cobalt, and nickel vapors do not give arene complexes with haloarenes. Interactions with hexafluorobenzene have been reported, but the explosive products are unlikely to be complexes containing planar C_6F_6 rings. The $\text{Ni-C}_6\text{F}_6$ cocondensate is a source of

"naked nickel," and the addition of ligands at low temperatures causes displacement of the hexafluorobenzene and formation of nickel complexes of the added ligands (58).

3. Other Aromatic Systems

Chromium atoms provide a unique route to π -pyridine complexes. No simple product has been isolated from the reaction of pyridine and chromium atoms, but 2,6-dimethylpyridine and chromium atoms give a low yield of $(\eta^6\text{-2,6-dimethylpyridine})_2\text{chromium}$ characterized by a crystal structure showing essentially planar pyridine rings (103). A mixture of pyridine with either PF_3 or mesitylene gives a $\pi\text{-C}_5\text{H}_5\text{N}$ complex:



In both reactions the yield of product is low. With PF_3 , some $\text{Cr}(\eta^1\text{-C}_5\text{H}_5\text{N})(\text{PF}_3)_5$ is formed in addition to the complex, but the two compounds are easily separated by chromatography (78, 83). Conventional synthetic methods can form complexes of type $\text{Cr}(\text{alkylpyridine})(\text{CO})_3$ but not the complexes of $\text{C}_5\text{H}_5\text{N}$ or $\text{Cr}(\eta^6\text{-alkylpyridine})_2$ (81).

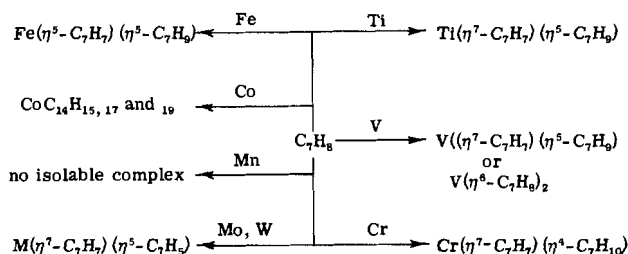
Hexamethylborazene, chromium vapor, and PF_3 together give a low yield of $\text{Cr}(\eta^6\text{-B}_3\text{N}_3\text{Me}_6)(\text{PF}_3)_3$. Attempts to isolate a bisborazenechromium complex were not successful (83).

It seems likely that thiophene-metal π -complexes are formed when thiophene is condensed with iron vapor, but the products isolated indicate subsequent desulfurization of the thiophene by the metal (18, 41) (see Section IV,B).

C. Polyenes

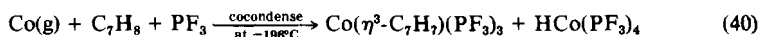
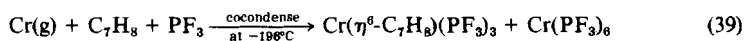
1. Cycloheptatriene

The reactions of cycloheptatriene with transition metal atoms are similar to those of cyclopentadiene. In both cases, the reactions can involve extensive migration of hydrogen in the formation of the final product (9, 10, 133, 136):



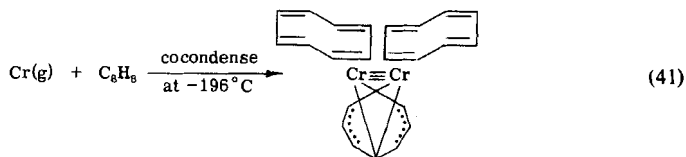
It is of interest that identical products to those derived from the metal atom technique are produced by the reduction of the metal halide (Co, Fe, Cr, V, and Ti) with Pr^iMgBr in the presence of cycloheptatriene (27, 85, 137). There are tentative reports of the formation of an unstable complex with chromium, possibly $\text{Cr}(\eta^6\text{-C}_7\text{H}_8)_2$, but these have not yet been confirmed (115, 140).

The reactions of cycloheptatriene with metal vapors may be altered by the addition of other ligands (133, 140):



2. Cyclooctatetraene

The reaction of cyclooctatetraene with metal atoms has not produced the same range of complexes as has 1,5- C_8H_{12} , C_5H_6 , or C_7H_8 . This can be ascribed to the ease of the metal-assisted polymerization of C_8H_8 and to the ready formation of metal-containing polymers by subsequent reactions of the free olefinic bonds in coordinated C_8H_8 . Thus, it is found that Ti, Fe, and Co atoms react with C_8H_8 to afford intractable polymers, even though the systems $\text{Ti}(\text{C}_8\text{H}_8)_2$, $\text{Ti}_2(\text{C}_8\text{H}_8)_3$, $\text{Fe}(\text{C}_8\text{H}_8)_2$, and $\text{Co}(\text{C}_8\text{H}_8)(\text{C}_8\text{H}_9)$ are known to be stable (14, 17, 34, 134). However, in some metal atom reactions discrete organometallic products can be obtained (133), e.g.,

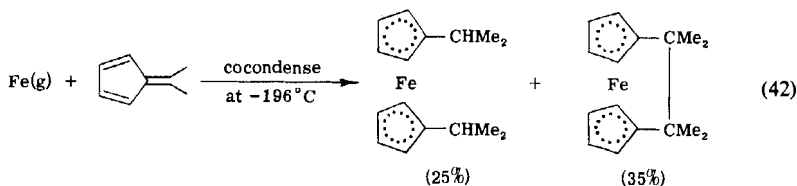


Condensation of uranium vapors with C_8H_8 affords uranocene, $\text{U}(\text{C}_8\text{H}_8)_2$ (33). However, this may not be a metal *atom* reaction: simply by vaporizing and condensing uranium vapor by itself would afford

highly activated bulk metal, which is known to afford $U(C_8H_8)_2$ with C_8H_8 (119). Interestingly, the reverse reaction, the decomposition of $U(C_8H_8)_2$ to uranium atoms and C_8H_8 can be brought about by bombardment of $U(C_8H_8)_2$ with excited argon atoms, and it does seem to be a practical route to generating U atoms (77). Lanthanide atoms react with C_8H_8 to afford $Ln_2(C_8H_8)_3$. The molecular structure of the THF adduct of one of these complexes, $[Nd(C_8H_8)(THF)_2][Nd(C_8H_8)_2]$, has been shown to contain asymmetrically bound C_8H_8 ligands (25a).

3. Other Polyenes

Direct reaction of fulvenes with metal atoms appears to afford a useful synthetic route to alkyl-bridged metallocenes (122), e.g.,



Azulenes and related polyenes also react with metal atoms but no details are as yet known (29, 102).

IV

INSERTION REACTIONS OF METAL ATOMS

Metal atoms are oxidized on interaction with many compounds containing polar bonds $R-X$. This effect has already been noted in Section III in reactions of metal atoms with arenes containing electronegative substituents. The products of oxidation that can be isolated are of three types, namely, RMX , RM , and $R_2 + MX$; unstable organometallic products can be sometimes stabilized by addition of a ligand, L , at low temperatures to give $RM(L_n)X$ or RML_n .

Most work has been done with carbon-halogen compounds and these are considered first.

A. Carbon-Halogen Compounds

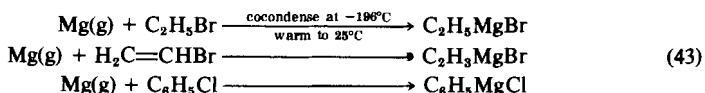
The strength of carbon-halogen bonds decreases more from $C-F$ to $C-I$ than the corresponding decrease from $M-F$ to $M-I$ in most

metal halides. Thus, whereas only the most electropositive metals, e.g., calcium, will attack C—F bonds, most metal atoms attack C—I bonds, with C—Cl and C—Br bonds showing intermediate behavior. The perfluoroorganic moiety of perfluoroorganic halides is inert to vapors of metals such as nickel or palladium that will insert only into C—Cl, C—Br, or C—I bonds.

The reactivity of metal atoms toward carbon-halogen bonds is also affected by the nature of the rest of the molecule: carbon-halogen bonds in unsaturated compounds are generally more reactive than those in saturated compounds.

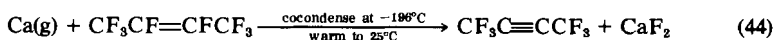
1. Main Group Metal Reactions

The first organometallic compounds from oxidation of metal atoms were reported by Skell and Girard (106). They evaporated magnesium from a crucible at 500°C and condensed the vapor with a range of straight-chain and branched-chain alkyl halides. The condensates at -196°C were black but became colorless on warming as the products RMgX, unsolvated Grignard reagents, were formed, e.g.,



The yields were excellent except in the case of Bu^tBr which gave only a 5% yield of Bu^tMgBr. The unsolvated Grignard reagents are stronger Lewis acids than the normal solvated products. Thus, *n*-C₃H₇MgBr enolizes acetone with elimination of propane rather than forming (CH₃)₂(C₃H₇)COH. Evaporation of magnesium from an arc yields excited atoms that tend to create alkyl radicals by halogen abstraction rather than by insertion into the carbon-halogen bonds (110).

Klabunde *et al.* (66) reported that calcium atoms react with unsaturated perfluoroorganic compounds, but there is no reaction with perfluoroalkanes. Organocalcium compounds were not isolated, but their presence was inferred from reactions of the condensates at low temperatures. The final products on warming to room temperature were calcium fluoride and defluorinated organic compounds, e.g.,



(cf. Pd + CF₃CF=CFCF₃ in Section II,A,4).

Zinc atoms react with CF₃I to give a product that behaves chemically as if it could be CF₃ZnI but the compound was too unstable to isolate (62). Decomposition of the CF₃ZnI yields C₂F₆ and C₂F₄ presumably via radicals.

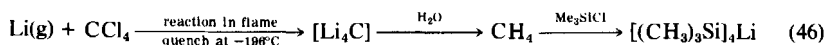
Germanium vapor (which may contain molecular species as well as Ge atoms) gives small yields of $\text{CCl}_3\text{GeCl}_3$ and $\text{HCCl}_2\text{GeCl}_3$ with CCl_4 and HCCl_3 , respectively (80).

Surprisingly, tin vapor fails to react on condensation with alkyl chlorides or bromides. It will react with some alkyl iodides; thus, with methyl iodide, a high yield of polymeric MeSnI is obtained together with very small yields of volatile methylodostannanes. Allyl chloride gives $\text{Sn}(\text{C}_3\text{H}_5)_3\text{Cl}$ in moderate yield. The reaction with HCl and acetylene is more complex, the intermediate may be H-Sn-Cl :



Generally, tin vapor appears only slightly more reactive than finely divided tin in its reactions with organic halides (83).

Lagow has carried out reactions between lithium atoms and organohalogen compounds in the gas phase (19, 20). For example, when CCl_4 vapor was bled into a dense stream of lithium vapor and the mixture condensed at -196°C , the condensate behaved chemically as if it contained Li_4C , e.g.,



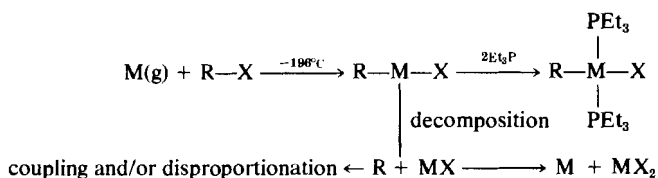
Perlithiated organic compounds also seem to have been formed in a similar way from alkyl halides and lithium vapor, presumably by loss of hydrogen as LiH ; 1-bromopropane and lithium vapor on condensation gave a product that yielded mainly C_3D_8 with some C_2D_6 , $\text{CD}_3\text{CD}=\text{CD}_2$, and $\text{CD}_3\text{C}\equiv\text{CD}$ on deuterolysis.

2. Transition Metal Reactions

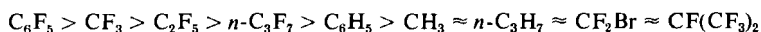
The most systematic study of reactions of transition metal atoms with halogen compounds has been the work of Klabunde on oxidation of nickel and palladium atoms. Some work has been done with copper, silver, gold, and platinum, but only scattered results have been reported for other metals. Klabunde's research has shown that perfluoroorganohalides form isolable organometallic compounds on reaction with metal atoms much more commonly than nonfluorinated halides. The types of reactions observed with different classes of organic halides are considered next.

a. Alkyl and Aryl Halides and Their Perfluoro Derivatives. Nickel and palladium atoms insert into the R-X bond of a wide range of alkyl, aryl, perfluoroalkyl, and perfluoroalkyl and perfluoroaryl chlorides, bromides, and iodides. The insertion product, RMX is often unstable except at very low temperatures and decomposes on warming. How-

ever, it can sometimes be stabilized by complexation with a phosphine ligand. Klabunde has represented the processes as follows (54):



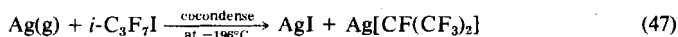
The initial insertion products with palladium are generally much more stable than those with nickel. Thus, $\text{C}_6\text{F}_5\text{PdX}$, CF_3PdX , and $\text{C}_2\text{F}_5\text{PdI}$ are stable at room temperature, whereas the corresponding nickel compounds decompose above -80°C (54, 64). The decomposition temperature for the unstable species has been assessed by finding the highest temperature at which addition of a phosphine traps the unstable species as a stable phosphine complex. The sequence of stability of RMX for different alkyl and aryl groups determined by Klabunde is



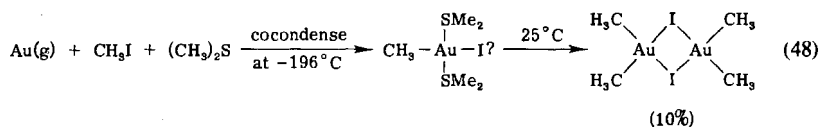
The difference in stability between $n\text{-C}_3\text{F}_7\text{PdI}$, which is stable at room temperature, and $i\text{-C}_3\text{F}_7\text{PdI}$, which decomposes above -78°C , is particularly striking. The opposite order of stability, i.e., $i\text{-C}_3\text{F}_7$ more stable than $n\text{-C}_3\text{F}_7$, is observed for compounds of type AgR_F , which are considered later in this section. These effects have not yet been properly explained.

The yields of insertion products with nickel or palladium atoms are low, usually less than 25% even with a very large excess of RX . The yields are highest with iodides and lowest with chlorides as expected from thermodynamic considerations (see preceding).

The behavior of the copper group metals toward RX is rather different from that of nickel and palladium. Organometallic products have been isolated in only a few cases so far. Silver atoms react with $i\text{-C}_3\text{F}_7\text{I}$,

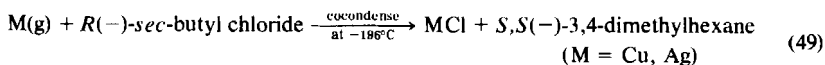


The silver compound is stable at room temperature but the corresponding $n\text{-C}_3\text{F}_7$ and CF_3 compounds appear to decompose above -100°C . Mention is also made of CuC_6F_5 and AgC_6F_5 being formed in analogous reactions (57). Gold atoms react with methyl iodide in the presence of dimethylsulfide:

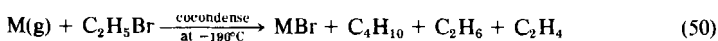


The role of the dimethylsulfide is not clear, but if it is not present only ethane is formed (43).

In other reactions of copper and silver atoms with RX, only dehalogenation has been observed. However, the reactions occur in high yield and are stereospecific, e.g.,

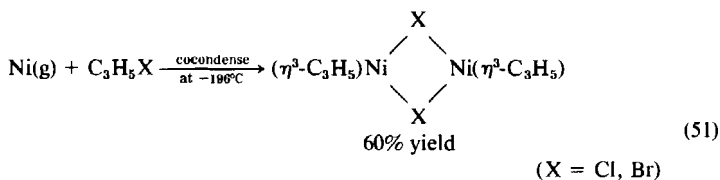


With ethyl bromide, the relative proportions of coupled and disproportionated product from the ethyl radicals are different for the reactions with copper, silver, and gold vapors, i.e.,

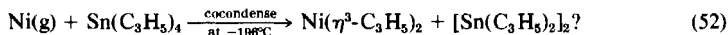


for M = Cu, it is mostly C_4H_{10} ; for M = Ag, it is mostly $C_2H_6 + C_2H_4$; and for M = Au, the amounts are equal (4).

b. Allyl and Benzyl Halides and Perfluoro Derivatives. In contrast to the low-yield reactions with alkyl halides, reactions of the nickel group elements with allyl halides are very efficient. Presumably there is an initial interaction between the atom and the $C=C$, which then permits the thermodynamically favored metal insertion reaction to proceed, e.g. (93),



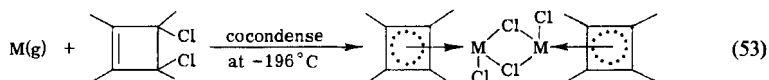
Bis(π -allyl)nickel is not formed in this reaction, but the compound can be made by condensing nickel vapor with tetraallyltin (131):



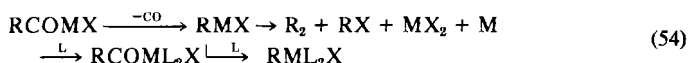
Palladium atoms react like nickel atoms toward allyl halides, but the reaction between Pt atoms and allyl chloride gives the tetramer $(\eta^3\text{-}C_3H_5PtCl)_4$ (107).

Toward palladium atoms, benzyl chloride or bromide behave like allyl halides giving very stable compounds $(\eta^3\text{-}C_6H_5CH_2PdX)_2$. Phosphines convert the benzyl group from being π -bonded to being σ -bonded forming, for example, $Pd(PEt_3)_2(CH_2C_6H_5)Cl$ (55, 97).

Cyclobutadiene complexes can also be made by metal atom reactions. For example, the reaction of 3,4-dichloro-1,2,3,4-tetramethylcyclobut-1-ene with nickel or palladium atoms (133) is



c. *Acyl Halides*. Nickel and palladium atoms appear to form organo-metallic compounds, $RCOMX$, on reaction with acyl or perfluoroacyl halides (64). None of the compounds has been isolated in a pure state, but in a few cases they have been stabilized with ligands as complexes, $RCOML_2X$. The mode of decomposition of the compounds can be represented as follows:

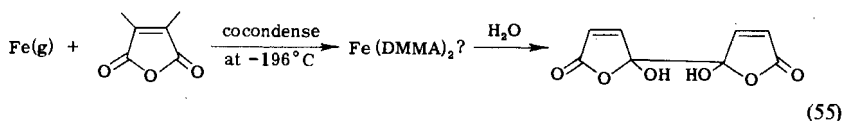


The stability of $RCOMX$ decreases in the sequence $R = n\text{-C}_3\text{F}_7 > \text{CF}_3 > \text{C}_6\text{F}_5 > \text{C}_6\text{H}_5 > \text{CF}_3\text{CH}_3$.

B. Other Insertion and Oxidation Reactions

The work on reactions of metal atoms with organic halides shows that this is a rich field. Comparable reactions occur between transition metal atoms and many oxygen and sulfur-containing compounds although published details are still sparse.

Metal atoms are oxidized by compounds containing carbonyl or hydroxy groups. Thus, a range of metal atoms (Cr, Mn, Fe, Ni, Cu, Zn, Al, Sn, and Pb) have been condensed with acetylacetone. In each case the product isolated was the metal acetylacetonate in yields of 10 to 30%. Iron initially gave $\text{Fe}(\text{acac})_2$ which was oxidized to $\text{Fe}(\text{acac})_3$ on exposure to air in the presence of excess acetylacetone (9, 140). Aldehydes give alcohols, coupled diols, or hydrocarbons depending on the metal used (29). The reaction of methanol and chromium atoms gives $\text{Cr}(\text{OCH}_3)_3$, and with acetic acid a mixture of chromium(II) and chromium(III) acetates are formed (140). Manganese atoms react extremely efficiently with acetic anhydride to form a complex Mn(II) acetate (6). Iron atoms induce coupling between dimethyl maleic anhydride (DMMA) molecules (140):

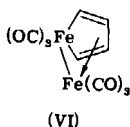


Few, if any, of the foregoing reactions involve the formation of true organometallic compounds even as intermediates, but there is much

scope in this area for developing useful organic syntheses from metal atom reactions.

The reaction between metal atoms and ethers is varied. Deoxygenation occurs with the more electropositive transition metals, e.g., Ti, V, Cr, and probably Fe, but Klabunde has been able to use tetrahydrofuran as a medium to form active nickel slurries by condensing in nickel vapor (56, 60).

Thiophenes are desulfurized by chromium and iron atoms. The role of complex intermediates is uncertain but with iron the final product appears to be a ferracyclopentadiene derivative (18):



V

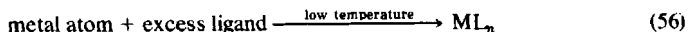
DISCUSSION

There is now a substantial body of results from synthetic reactions with metal atoms. From these it is possible to draw some broad guidelines as to the expected yields of products in metal atom reactions and to make a comparison of the usefulness of metal atom synthetic techniques with other methods for preparing organometallic compounds.

A. Yields of Products

When metal atoms condense on a surface, the recombination to form bulk metal will occur at a rate controlled only by diffusion even at 4 K. Thus, any desired atom-molecule reaction occurring on cocondensation must be very facile to compete with metal polymerization.

Fortunately, most metal atom-ligand interactions appear to have a low activation energy. Many simple reactions of the type

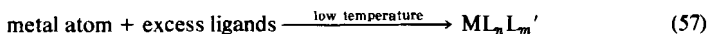


give yields of product in the range 20–60%, depending on the metal vapor condensed, when the metal-to-ligand mole ratio is at a practicable level, e.g., 1:10 to 1:50. The larger the excess of ligand the larger the yield based on metal vaporized. If the product is very thermally unstable, it may not be possible to isolate it, but the yield can be

established by converting the product into another, more stable compound by low-temperature reactions.

A few reactions will give yields in the range 20–60% only if the rate of condensation metal vapor is kept low. In these cases, rapid deposition of metal seems to create aggregates that can catalyze the decomposition of the desired product, e.g., $\text{Ti} + \text{C}_6\text{H}_6$ and Fe , Co , or $\text{Pd} + 1,5\text{-COD}$ (see Sections III,A and B).

In the formation of complexes containing two different ligands by reactions of the type,



the yield of $\text{ML}_n\text{L}_m'$ will commonly be in the range 10–20%; the formation of ML_{n+m} and ML_{n+m}'' will be competing processes reducing the yield of mixed product.

The main cause of low yields of reaction products in metal atom–ligand reactions is competing reactions. These include unwanted halogen abstraction reactions, such as polymerization of the ligand (84), e.g., $\text{Fe} + \text{COT}$ (133), or competing complexation, e.g., $\text{Cr} + \text{dimethylpyridine}$ (103). It is rarely possible to eliminate the effect of these side reactions although the use of a very large excess of the ligand may reduce ligand polymerization effects.

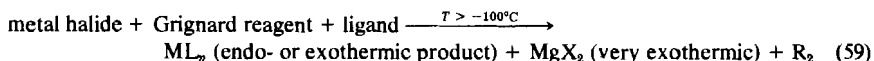
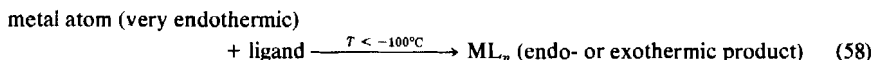
Metal atom syntheses that depend on bond insertion reactions are more likely to be affected by activation energy barriers than metal atom–ligand reactions. Thus, no example has yet been reported of insertion of metal atoms into single $\text{C}-\text{C}$ bonds and insertion occurs only into activated $\text{C}-\text{H}$ bonds. As discussed in Section IV,A, the insertion of transition metal atoms into allyl–halogen bonds is much more efficient than into alkyl–halogen bonds: an initial π -acid–base interaction of the metal atom with the $\text{C}=\text{C}$ of the allyl group will have a much lower activation energy than the bond insertion process. Far wider variations in yields are observed with insertion reactions than with metal atom–ligand reactions. Hydrogen migration is common in reactions of metal atoms. Where there is an intramolecular process, e.g., in the reaction of nickel atoms and C_5H_8 (93), or where there is intermolecular hydrogen transfer to from a metal hydride as in the reaction of cobalt atoms, PF_3 , and C_3H_8 (131), the yield of product can be very high. With intermolecular hydrogen abstraction, e.g., in the formation of $(\text{C}_7\text{H}_{10})\text{Cr}(\text{C}_7\text{H}_7)$ (133), the process is often inefficient and the yield of product low.

In theory, a metal atom–substrate reaction that has a higher activation energy than the polymerization of the metal atoms can be made more competitive in rate if the temperature is raised. This is not always practicable in atom chemistry because of the need to keep the vapor

pressures of the components low, but a growing number of examples are being found where reactions give higher yields if the temperature of condensation is raised from -196°C to about -130°C . The rotary solution reactor (Fig. 3) is particularly useful in allowing higher temperatures to be used with a useful gain in yields of products in some cases.

B. Comparison of Metal Atom with Other Synthetic Methods

It is interesting to compare the scope of metal atom synthesis with more established methods of making organometallic compounds. The comparison is simplest when considering the formation of zero-valent complexes, ML_n . Such compounds are often made by reducing a metal salt in the presence of the ligand, the most widely used reducing agents being aluminum alkyls, Grignard reagents, and alkali metals. The two types of processes, direct reactions with a metal atom and reduction of a metal salt, may be represented as follows:



With the metal atom reaction, the atom is the source of energy that allows the formation of either endothermic or exothermic products. With the reduction, the formation of the magnesium halide is the main source of energy.

The two types of reaction often give the same product. There are notable exceptions, however. There is no conventional access to such systems as $\text{M}(1,5\text{-COD})_2$ ($\text{M} = \text{Fe}, \text{Co}$), $\text{M}(\text{arene})_2$ ($\text{M} = \text{Ti}, \text{Nb}$), and $\text{M}(\text{C}_4\text{H}_6)$ ($\text{M} = \text{Mo}, \text{W}$) (see Section III). The reason for this is partly kinetic in that the metal atom is completely sterically accessible to the incoming ligand, not requiring the prior ligand dissociation or activation often found in conventional syntheses. The other factor is that any endothermicity of the products is more than offset by the usable energy supplied to the whole system by vaporization of the metal. This often provides much more energy to the system than is obtainable in conventional reductive synthesis, and, for this reason (along with the very low temperature employed), it is possible to prepare compounds far too endothermic for conventional access. Instead one of the major problems in metal atom synthesis is not in making highly endothermic systems but in devising methods to isolate such complexes. Generally this limitation is brought about by the reactivity and thermal instability of the products

under the conditions of work-up. In reactions in which the products are exothermic, including most bond insertion reactions, the primary advantage lies in the "nakedness" of the metal atoms. For example, the systems $R-M-X$ and $RCO-M-X$ ($R = CF_3-$, C_6F_5- , $C_6H_5CH_2-$, etc.) in which there are no other stabilizing ligands (CO , PR_3 , etc.) are relatively easy to prepare by the metal atom technique. The reactivity of even those metals with rather low heats of atomization, such as magnesium or zinc, is greater in the atomic form than for the bulk metal due mainly to kinetic factors.

A recent development of work with metal vapors, which lies between atom chemistry and conventional synthetic chemistry, is the preparation of reactive metal slurries. When a metal vapor is condensed with an inert organic compound, e.g., an alkane or sometimes an ether, and the condensate is allowed to warm to room temperature, the resultant slurry contains metal in a reactive form. It is less reactive than the metal atoms because aggregation of the atoms has occurred and is comparable in reactivity to active forms of metal produced by other methods, e.g., Raney nickel. The catalytic and synthetic potential of these metal slurries is being explored (55, 60).

The major limitations of the atom method are the scale of synthesis that is practicable and the inflexibility of reaction conditions. Apparatus that is easily handled and not too expensive to assemble or purchase can be used typically with up to 5 gm of a metal per run. Except for a few "easy" reactions, work on a larger scale, e.g., 50 gm of metal, requires more elaborate apparatus. It is not possible to change reaction conditions in atom chemistry in the same way as in conventional synthetic chemistry. The ligand has to be present in large excess and the temperature of reaction usually has to be low to maintain a high vacuum. Fortunately, within these constraints many reactions can be carried out successfully, and we expect to see a metal atom apparatus as a standard item of equipment in most laboratories making new organometallic compounds.

VI

APPENDIX: TABLES OF METAL VAPOR REACTIONS

List of abbreviations used in the tables:

1. *Methods of Reacting Atoms and Compounds*
- CC Cocondensation of the vapor of a compound and a metal vapor formed by thermal evaporation of a metal

CE	Cocondensation of the vapor of a compound and a metal vapor formed by electron bombardment heating of the metal.
CL	Cocondensation of the vapor of a compound and a metal vapor formed by laser beam evaporation of the metal
CT	Cocondensation of the vapor of a compound and a metal vapor in a thin layer for infrared spectroscopic studies
RE	Condensation of a metal vapor into a solution of a compound in a rotary evaporator apparatus
MI	Matrix isolation spectroscopic studies of metal atom reactions

2. Chemicals

acac	Acetylacetonate
CHD	1,3- or 1,4-Cyclohexadiene (specified)
CHT	Cycloheptatriene
COD	1,3- or 1,5-Cyclooctadiene (specified)
COT	Cyclooctatetraene
Cp	Cyclopentadienyl
DBA	Dibenzylideneacetone
DMMA	Dimethylmaleic anhydride
nb	Norbornene
nbd	Norbornadiene
THF	Tetrahydrofuran

TABLE I
GROUP IIIB

Metal	Substrate	Method	Product	Comments	References
Pr	CO	MI	$\text{Pr}(\text{CO})_n$	$n = 1-6$	100
Nd	CO	MI	$\text{Nd}(\text{CO})_n$	$n = 1-6$	100
Nd	COT	CC	$\text{Nd}_2(\text{COT})_3 \cdot 2\text{THF}$	THF extract	25a
Gd	CO	MI	$\text{Gd}(\text{CO})_n$	$n = 1-6$	100
Dy	Hacac	CL	$\text{Dy}(\text{acac})_3$	—	9,140
Ho	CO	MI	$\text{Ho}(\text{CO})_n$	$n = 1-6$	100
Ho	Hacac	CL	$\text{Ho}(\text{acac})_3$	—	9,140
Er	Hacac	CL	$\text{Er}(\text{acac})_3$	—	9,140
Yb	CO	MI	$\text{Yb}(\text{CO})_n$	$n = 1-6$	100
U	CO	MI	$\text{U}(\text{CO})_n$	$n = 1-6$	100,117
U	COT	CC	$\text{U}(\text{COT})_2$	—	33

TABLE II
GROUP IVB

Substrate	Method	Product (% yield)	References
a. Titanium			
C_6H_6	CE, CT	$Ti(C_6H_6)_2$ (ca. 30)	4a, 7
C_6H_5Me	CE	$Ti(C_6H_5Me)_2$ (ca. 30)	4a, 7
Mesitylene	CE	$Ti(C_6H_3Me_3)_2$ (ca. 30)	4a, 7
CHT	CC	$Ti(\eta^7-C_7H_7)(\eta^5-C_7H_9)$ (46)	133
No isolable organometallic products with C_6F_5Br (54), C_6F_6 (58), 1,5-COD (134), 1,3- C_4H_6 (1, 2), ferrocene, indene, C_5H_6 , and COT (134).			
b. Zr and Hf			
Propene does not yield an isolable organometallic product with Zr (107). No reactions of Hf have been reported.			

TABLE III
GROUP VB

Substrate	Method	Product (% yield)	Comments	References
a. Vanadium				
CO	MI	$V(CO)_n$, $V_2(CO)_{12}$	$n = 1-6$	27a, 84a
C_6H_6	CC	$V(C_6H_6)_2$ (2)	—	59
C_5H_5F	CC	$V(C_5H_5F)_2$ (13)	—	59
C_6H_5Cl	CC	$V(C_6H_5Cl)_2$ (7)	—	59
$C_6H_5CF_3$	CC	$V(C_6H_5CF_3)_2$ (1)	—	59
$p-C_6H_4F_2$	CC	$V(p-C_6H_4F_2)_2$ (1)	—	59, 94a
CHT	CC	$VC_{14}H_{16}$ (51)	$V(\eta^6-C_7H_8)_2$ or $V(\eta^7-C_7H_7)(\eta^5-C_7H_9)$	133
No isolable organometallic products with C_6F_6 (55, 58), m - or p - $C_6H_4(CF_3)_2$ (59), or 1,3- C_4H_6 (1).				
b. Tantalum				
CO	MI	$Ta(CO)_n$	$n = 1-6$	24
c. Niobium				
C_6H_6	MI	$Nb(C_6H_6)_2$	—	36

TABLE IV
GROUP VIB

Substrate	Method	Product (% yield)	Comments (% yield)	References
a. Chromium				
CO	MI	$\text{Cr}(\text{CO})_n$	$n = 1-6$, also $\text{Cr}_2(\text{CO})_x$	15, 30, 73, 74
CO/THF	CL	$\text{Cr}(\text{CO})_6$ (2.3)	—	140
1,3-COD	CL	?	+ CO \rightarrow $\text{Cr}(1,5\text{-COD})(\text{CO})_4$ (3)	140
1,3-COD/ PF_3	CL	$\text{CrH}(\eta^5\text{-C}_5\text{H}_{11})(\text{PF}_3)_3$ (1)	—	140
1,5-COD	CL	?	+ CO \rightarrow $\text{Cr}(1,5\text{-COD})(\text{CO})_4$ (8.5)	140
1,5-COD/ PF_3	CL	$\text{Cr}(1,5\text{-COD})(\text{PF}_3)_4$ (1) + $\text{CrH}(\eta^5\text{-C}_5\text{H}_{11})(\text{PF}_3)_3$ (2)	—	140
1,3- C_4H_6	CL	?	+ CO \rightarrow $\text{Cr}(1,3\text{-C}_4\text{H}_6)(\text{CO})_4$ (4.4)	140
1,3- $\text{C}_4\text{H}_6/\text{PF}_3$	CC	$\text{Cr}(1,3\text{-C}_4\text{H}_6)(\text{PF}_3)_4$ (3)	$T_{\text{dec}} = \text{ca. } 20^\circ\text{C}$	115
C_5H_6	CC	$\text{Cr}(\text{C}_5\text{H}_5)_2$ (50)	H_2 evolved $> -100^\circ\text{C}$	49, 115, 129
	CC	$[\text{Cr}(\text{C}_5\text{H}_5)_2\text{H}_2]?$	+ CO \rightarrow $\text{Cr}(\text{C}_5\text{H}_5)(\text{C}_5\text{H}_7)(\text{CO})_2$	50
C_6H_6	CC, MI	$\text{Cr}(\text{C}_6\text{H}_6)_2$ (60)	—	13, 32, 127, 130
$\text{C}_6\text{H}_5\text{Me}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Me})_2$ (60)	—	32, 115
$\text{C}_6\text{H}_5\text{Et}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Et})_2$ (52)	—	32, 115
$\text{C}_6\text{H}_5\text{Pr}^n$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Pr}^n)_2$ (16)	—	32
$\text{C}_6\text{H}_5\text{Pr}^i$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Pr}^i)_2$ (19)	—	32, 80, 84
$\text{C}_6\text{H}_5\text{Bu}^n$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Bu}^n)_2$ (14)	—	32
$\text{C}_6\text{H}_5\text{Bu}^i$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Bu}^i)_2$ (7)	—	32
$\text{C}_6\text{H}_5\text{Bu}^t$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Bu}^t)_2$ (27)	—	32
$\text{C}_6\text{H}_5\text{-C}_6\text{H}_{11}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{-C}_6\text{H}_{11})_2$ (14)	—	32
$\text{C}_6\text{H}_5\text{F}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{F})_2$ (19)	—	32, 79, 115
$\text{C}_6\text{H}_5\text{Cl}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{Cl})_2$ (47)	—	32, 115
$\text{C}_6\text{H}_5\text{CF}_3$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{CF}_3)_2$ (26)	—	32, 59
$\text{C}_6\text{H}_5\text{COOMe}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{COOMe})_2$ (4)	—	32
$\text{C}_6\text{H}_5\text{COOEt}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{COOEt})_2$ (10)	—	95a
$\text{C}_6\text{H}_5\text{OMe}$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{OMe})_2$ (8)	—	32
$\text{C}_6\text{H}_5\text{OC}_6\text{H}_5$	CC	$\text{Cr}(\text{C}_6\text{H}_5\text{OC}_6\text{H}_5)_2$ (3)	—	32

$C_6H_5NMe_2$	CC	$Cr(C_6H_5NMe_2)_2$ (6)	—	32
$C_6H_5CH=CH_2$	CC	complex polymers	—	9a
<i>o</i> - $C_6H_4Me_2$	CC	$Cr(o-C_6H_4Me_2)_2$ (25)	—	32
<i>m</i> - $C_6H_4Me_2$	CC	$Cr(m-C_6H_4Me_2)_2$ (25)	—	32
<i>p</i> - $C_6H_4Me_2$	CC	$Cr(p-C_6H_4Me_2)_2$ (29)	—	32
Indene	CC	$Cr(indene)_2$ (17)	—	32
<i>m</i> - $C_6H_4Pr_2^i$	CC	$Cr(m-C_6H_4Pr_2)_2$ (18)	—	83, 84
<i>m</i> - $C_6H_4(CF_3)_2$	CC	$Cr[m-C_6H_4(CF_3)_2]_2$ (17)	—	59
<i>p</i> - $C_6H_4(CF_3)_2$	CC	$Cr[p-C_6H_4(CF_3)_2]_2$ (38)	—	59
<i>o</i> - C_6H_4MeF	CC	$Cr(o-C_6H_4MeF)_2$ (16)	—	32, 79
<i>m</i> - C_6H_4MeF	CC	$Cr(m-C_6H_4MeF)_2$ (16)	—	32, 79
<i>p</i> - C_6H_4MeF	CC	$Cr(p-C_6H_4MeF)_2$ (21)	—	32, 79
<i>o</i> - C_6H_4MeCl	CC	$Cr(o-C_6H_4MeCl)_2$ (10)	—	32
<i>m</i> - C_6H_4MeCl	CC	$Cr(m-C_6H_4MeCl)_2$ (5)	—	32
<i>p</i> - C_6H_4MeCl	CC	$Cr(p-C_6H_4MeCl)_2$ (20)	—	32
<i>p</i> - $C_6H_4MeCOOMe$	CC	$Cr(p-C_6H_4MeCOOMe)_2$ (12)	—	32
<i>m</i> - $C_6H_4(CF_3)F$	CC	$Cr[m-C_6H_4(CF_3)F]_2$ (20)	—	32, 79
<i>o</i> - $C_6H_4(CF_3)Cl$	CC	$Cr[o-C_6H_4(CF_3)Cl]_2$ (33)	—	32, 59
<i>o</i> - $C_6H_4F_2$	CC	$Cr(o-C_6H_4F_2)_2$ (17)	—	79
<i>m</i> - $C_6H_4F_2$	CC	$Cr(m-C_6H_4F_2)_2$ (18)	—	32, 79
<i>p</i> - $C_6H_4F_2$	CC	$Cr(p-C_6H_4F_2)_2$ (12)	—	32, 79, 115
<i>o</i> - C_6H_4FCl	CC	$Cr(o-C_6H_4FCl)_2$ (23)	—	79
<i>m</i> - C_6H_4FCl	CC	$Cr(m-C_6H_4FCl)_2$ (17)	—	79
<i>p</i> - C_6H_4FCl	CC	$Cr(p-C_6H_4FCl)_2$ (17)	—	79
<i>p</i> - $C_6H_4Cl_2$	CC	$Cr(p-C_6H_4FCl)_2$ (17)	—	79
<i>m</i> - $C_6H_4Cl_2$	CC	$Cr(m-C_6H_4Cl_2)_2$ (10)	—	32
1,2,3- $C_6H_3Me_3$	CC	$Cr(1,2,3-C_6H_3Me_3)_2$ (5)	—	32
1,3,5- $C_6H_3Me_3$	CC	$Cr(1,3,5-C_6H_3Me_3)_2$ (13)	—	32
1,2,4- $C_6H_3Me_3$	CC	$Cr(1,2,4-C_6H_3Me_3)_2$ (5)	—	32
1,2,3,4- $C_6H_2Me_4$	CC	$Cr(1,2,3,4-C_6H_2Me_4)_2$ (7)	—	32
1,2,4,5- $C_6H_2Me_4$	CC	$Cr(1,2,4,5-C_6H_2Me_4)_2$ (21)	—	32
C_6H_6/PF_3	CC	$Cr(C_6H_6)(PF_3)_3$ (15)	—	49, 84

(continued)

TABLE IV—(Continued)

Substrate	Method	Product (% yield)	Comments (% yield)	References
$C_6H_5Pr^+/PF_3$	CC	$Cr(C_6H_5Pr^+)(PF_3)_3$ (27)	—	83, 84
$C_6H_5CH=CH_2/PF_3$	CC	$Cr(C_6H_5CH=CH_2)(PF_3)_3$ (trace)	—	83
$m-C_6H_4Pr_2^+/PF_3$	CC	$Cr(m-C_6H_4Pr_2^+)(PF_3)_3$ (17)	—	83, 84
Mesitylene/ PF_3	CC	$Cr(C_6H_3Me_3)(PF_3)_3$ (23)	—	83, 84
C_6F_6/PF_3	CC	$Cr(C_6F_6)(PF_3)_3$ (2)	—	83, 84
Napthalene/ PF_3	CC	$Cr(C_{10}H_8)(PF_3)_3$ (7)	—	83
C_6H_6/C_6F_6	CC	$Cr(C_6H_6)(C_6F_6)$ (1)	—	83
C_6H_6/C_6F_5H	CC	$Cr(C_6H_6)(C_6F_5H)$ (22)	—	124
		+ $LiBu^+ \rightarrow Cr(C_6H_5)(C_6F_5Li)$	—	124
C_6H_6/C_6H_5Cl	MI	$Cr(C_6H_6)(C_6H_5Cl)$	—	96
2,6- $Me_2C_5H_3N$	CC	$Cr(\eta^5-Me_2C_5H_3N)_2$ (2)	—	103
CHT	CC, CL	$Cr(\eta^5-C_7H_8)_2$	Not confirmed	115, 140
	CL, RE	$Cr(\eta^7-C_7H_7)(\eta^5-C_7H_{10})$ (17)	—	9, 133
CHT/ PF_3	CC, CL	$Cr(\eta^5-C_7H_8)(PF_3)_3$ (7)	—	9, 133
COT	CC	$Cr_2(COT)_3$ (43)	—	133
$Sn(allyl)_4$	CC	$Cr_2(C_3H_5)_6$	—	132
C_5H_5N/PF_3	CC	$Cr(C_5H_5N)(PF_3)_3$ (8)	σ -Bonded	83
		+ $Cr(C_5H_5N)(PF_3)_3$ (1)	π -Bonded	
$B_3N_3Me_6/PF_3$	CC	$Cr(B_3N_3Me_6)(PF_3)_3$ (3)	π -Bonded	83
Hacac	CL	$Cr(acac)_3$ (32)	—	9, 140
MeOH	CL	$Cr(OMe)_3$ (28) also Pr^+OH and Bu^+OH	—	140
MeCOOH	CL	$Cr(O_2CMe)_3$ (30)	$n = 2, 3$	140
PF_3	CC	$Cr(PF_3)_6$ (60)	—	120

No isolable organometallic products from C_6F_6 (58), 1,3- C_4H_6 (1, 136), propene, 1-butene, 1-pentyne (115), 1,3- or 1,4-CHD (110), $C_6(CF_3)_6$ / PF_3 , C_5H_5N/C_6H_5N , EtBr, dibutylphthalate (83), 1,5-COD (82, 140), 1,3-COD (140), PMe_3 , nbd, nb, $PbMe_4$ (134), or C_2H_4 (5a).

b. Molybdenum

CO	MI	$Mo(CO)_n$	$n = 1-6$	68
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1,3-C ₄ H ₆	CC	Mo(C ₄ H ₆) ₃ (50–60)	—	110, 114
C ₅ H ₈	CC	MoH ₂ (C ₅ H ₈) ₂ (30–50)	—	21, 136
C ₆ H ₆	CC, CE	Mo(C ₆ H ₆) ₂ (30–50)	—	7, 113
C ₆ H ₅ Me	CC, CE	Mo(C ₆ H ₅ Me) ₂ (30–50)	—	7, 113
C ₆ H ₅ F	CC	Mo(C ₆ H ₅ F) ₂ (30–50)	—	113
C ₆ H ₅ Cl	CC	Mo(C ₆ H ₅ Cl) ₂ (30–50)	—	113
C ₆ H ₅ COOMe	CC	Mo(C ₆ H ₅ COOMe) ₂ (30–50)	—	113
C ₆ H ₅ OMe	CC	Mo(C ₆ H ₅ OMe) ₂ (30–50)	—	113
C ₆ H ₅ NMe	CC	Mo(C ₆ H ₅ NMe) ₂ (30–50)	—	113
Mesitylene	CE	Mo(C ₆ H ₃ Me) ₃	—	7
Indene	CC	Mo(η ⁶ -C ₉ H ₈) ₂ + MoH ₂ (η ⁵ -C ₉ H ₇) + MoH(η ⁶ -C ₉ H ₈)(η ⁵ -C ₉ H ₇)	—	136
CHT	CC	Mo(η ⁷ -C ₇ H ₇)(η ⁵ -C ₇ H ₉)	—	136
PF ₃	CC	Mo(PF ₃) ₆	—	132

No isolable organometallic products from nbd (107, 110) or nb (102).

c. Tungsten

Cyclopentene	CC	WH ₂ (C ₅ H ₅) ₂	—	136
1,3-C ₄ H ₆	CC	W(C ₄ H ₆) ₃ (50–60)	—	110, 114
C ₅ H ₈	CC	WH ₂ (C ₅ H ₈) ₂ (40–60)	—	21, 136
C ₆ H ₆	CC	W(C ₆ H ₆) ₂ (30–50)	—	113
C ₆ H ₅ Me	CC	W(C ₆ H ₅ Me) ₂ (30–50)	—	113
C ₆ H ₅ OMe	CC	W(C ₆ H ₅ OMe) ₂ (30–50)	—	113
C ₆ H ₅ F	CC	W(C ₆ H ₅ F) ₂ (30–50)	—	113
<i>o</i> -C ₆ H ₄ Me ₂	CC	W(<i>o</i> -C ₆ H ₄ Me ₂) ₂ (30–50)	—	113
C ₆ H ₆ /C ₅ H ₆	CC	W(C ₆ H ₆) ₂ + WH ₂ (C ₅ H ₅) ₂ + WH(C ₆ H ₆)(C ₅ H ₅)	—	136
C ₆ H ₅ Me/C ₅ H ₆	CC	W(C ₆ H ₅ Me) ₂ + WH ₂ (C ₅ H ₅) ₂ + WH(C ₆ H ₅ Me)(C ₅ H ₅)	—	136
CHT	CC	W(η ⁷ -C ₇ H ₇)(η ⁵ -C ₇ H ₉) (20)	—	136
Indene	CC	W(η ⁶ -C ₉ H ₈) + WH ₂ (η ⁵ -C ₉ H ₇) ₂ + WH(η ⁶ -C ₉ H ₈)(η ⁵ -C ₉ H ₇)	—	136

No isolable organometallic products from nbd (102, 110) or nb (102).

TABLE V
GROUP VIIB

Substrate	Method	Product (% yield)	Comments	References
a. Manganese				
CO	MI	$\text{Mn}(\text{CO})_n + \text{Mn}_2(\text{CO})_x$	$n = 1-5, x = 1-10$	48
CO/THF	CL	$\text{Mn}_2(\text{CO})_{10}$ (1.0)	—	9, 140
$\text{C}_6\text{H}_6/\text{C}_5\text{H}_6$	CC, CL	$\text{Mn}(\text{C}_6\text{H}_6)(\text{C}_5\text{H}_5)$ (4)	—	6, 140
$\text{C}_6\text{H}_5\text{Me}/\text{C}_5\text{H}_6$	CC, CL	$\text{Mn}(\text{C}_6\text{H}_5\text{Me})(\text{C}_5\text{H}_5)$ (5)	—	6, 140
Mesitylene/ C_5H_6	CC	$\text{Mn}(\text{C}_6\text{H}_3\text{Me}_3)(\text{C}_5\text{H}_5)$	—	6
$\text{C}_6\text{H}_5\text{Me}/\text{C}_5\text{H}_5\text{Me}$	CL	$\text{Mn}(\text{C}_6\text{H}_5\text{Me})(\text{C}_5\text{H}_4\text{Me})$	—	140
Hacac	CL	$\text{Mn}(\text{acac})_2$ (30)	—	9, 140
$\text{PF}_3/\text{NO}/\text{BF}_3$	CC	$\text{Mn}(\text{NO})(\text{PF}_3)_3$ (5)	—	176
C_4H_6	CC	?	+ CO \rightarrow $\text{Mn}(\text{C}_4\text{H}_6)_2\text{CO}$	40
1,3-CHD	CC	?	+ CO \rightarrow $\text{Mn}(1,3\text{-CHD})_2\text{CO}$	75
1,3-COD	CC	?	+ CO \rightarrow $\text{Mn}(\eta^3\text{-C}_8\text{H}_{13})(\text{CO})_4$ + $\text{Mn}(\eta^5\text{-C}_8\text{H}_{11})(\text{CO})_3$	75
No isolable organometallic products from C_6H_6 , C_6F_6 (58), C_5H_6 , $\text{C}_5\text{H}_6/\text{C}_6\text{H}_5\text{Cl}$ (6), 1,3- C_4H_6 (1), C_7H_8 , C_7H_8 , $\text{C}_7\text{H}_8/\text{PF}_3$, PMe_3 , nb, or 1,5-COD (134).				
b. Rhenium				
CO	MI	$\text{Re}(\text{CO})_5$	—	68

TABLE VI
IRON TRIAD

Substrate	Method	Product (% yield)	Comments	References
a. Iron				
CO/THF	CL	$\text{Fe}(\text{CO})_5(0.4) + \text{Fe}_2(\text{CO})_9$ (trace) + $\text{Fe}_3(\text{CO})_{12}(0.2)$	—	9, 140
Propene/ PF_3 1,5-COD	CC	$\text{Fe}\eta^3\text{-C}_3\text{H}_5(\text{PF}_3)_3 + \text{H}_2\text{Fe}(\text{PF}_3)_4$	$T_{\text{dec}} = 20^\circ\text{C}$	28, 125
	CM, RE	$\text{Fe}(1,5\text{-COD})_2$ (40)	$T_{\text{dec}} = -30^\circ\text{C}$	81
	RE	$\text{Fe}(1,5\text{-COD})_2$ (40)	+ CO $\rightarrow \text{Fe}(\text{CO})_5 + \text{Fe}(1,5\text{-COD})(\text{PF}_3)_3$	16, 26
			+ $\text{Bu}'\text{NC} \rightarrow \text{Fe}(1,5\text{-COD})(\text{Bu}'\text{NC})_3$	16
			+ $\text{PF}_3 \rightarrow \text{Fe}(1,5\text{-COD})(\text{PF}_3)_3$	16
	CC, RE	$\text{Fe}(1,5\text{-COD})_2$ (40)	+ $\text{P}(\text{OMe})_3 \rightarrow \text{Fe}(1,3\text{-COD})[\text{P}(\text{OMe})_3]_3$	16, 26
	CC	$\text{Fe}(1,5\text{-COD})_2$ (40)	+ $\text{P}(\text{OEt})_3 \rightarrow \text{Fe}(1,3\text{-COD})[\text{P}(\text{OEt})_3]_3$	26
			+ $\text{P}(\text{OPr}^i)_3 \rightarrow \text{Fe}(1,3\text{-COD})[\text{P}(\text{OPr}^i)_3]_3$	26
			+ $\text{P}(\text{OCH}_2)_3\text{CEt} \rightarrow \text{Fe}[\text{P}(\text{OCH}_2)_3\text{CEt}]_5$	26
	RE	$\text{Fe}(1,5\text{-COD})_2$ (40)	+ COT $\rightarrow \text{Fe}(\text{COT})_2$	82
1,5-COD/ PF_3 1,3- C_4H_6			+ Diphos/ $\text{N}_2 \rightarrow \text{Fe}(\text{diphos})_2\text{N}_2$	82
			+ Diphos/CO $\rightarrow \text{Fe}(\text{diphos})_2\text{CO}$	82
			+ 1,3- C_4H_6 /CO $\rightarrow \text{Fe}(\text{C}_4\text{H}_6)_2\text{CO}$	16, 82
			+ 1,3- C_4H_6 / $\text{Bu}'\text{NC} \rightarrow \text{Fe}(\text{C}_4\text{H}_6)_2\text{Bu}'\text{NC}$	16
	CC	$\text{Fe}(1,5\text{-COD})(\text{PF}_3)_3$	—	16
1,3- C_4H_6	CC, CL	$\text{Fe}(\text{C}_4\text{H}_6)_n$	$n = 2 \text{ or } 3, T_{\text{dec}} = +5^\circ\text{C}$	82, 140, 143
	CC, CL	$\text{Fe}(\text{C}_4\text{H}_6)_n$	+ CO $\rightarrow \text{Fe}(\text{C}_4\text{H}_6)_2\text{CO}$	138, 143
	CC, CL	$\text{Fe}(\text{C}_4\text{H}_6)_n$	+ $\text{PF}_3 \rightarrow \text{Fe}(\text{C}_4\text{H}_6)_2\text{PF}_3$	138, 143
	CC	$\text{Fe}(\text{C}_5\text{H}_5)_2$ (60)	—	127
C_5H_6	CC	$\text{Fe}(\text{C}_5\text{H}_5)_2$ (trace)	—	38
Indene	CC	$\text{Fe}(\text{C}_6\text{H}_5)(1,3\text{-C}_6\text{H}_5)$ (1.7)	—	143

(continued)

TABLE VI—(Continued)

Substrate	Method	Product (% yield)	Comments	References
C_6H_6	CT	$Fe(C_6H_5)_2$	$T_{dec} = ca. -50^\circ C$	76
C_6H_6/PF_3	CC	$Fe(C_6H_5)(PF_3)_2(20)$	—	84
C_6H_5Me	CC, CT, RE	$Fe(C_6H_5Me)_2$	$T_{dec} = ca. -60^\circ C$	76, 134
	CC	$Fe(C_6H_5Me)_2$	$+ PF_3 \rightarrow Fe(C_6H_5Me)(PF_3)_2$	143
			$+ 1,3-C_4H_6 \rightarrow Fe(C_6H_5Me)(C_4H_6)$	143
			$+ 1,5-COD \rightarrow Fe(C_6H_5Me)(1,5-COD)$	41
			$+ COT \rightarrow Fe(C_6H_5Me)(COT)$	28
Mesitylene	CC, RE	$Fe(C_6H_5Me)_2$	—	82
	RE	$Fe(C_6H_5Me)_2$	—	10, 133
CHT	CL, RE	$Fe(\eta^5-C_7H_7)(\eta^5-C_7H_9) (15)$	—	122
6,6'-Dimethylfulvene	CC	$Fe(C_5H_4Pr^t)_2 (25)$ $+ (FeC_5H_4CMe_2)_2 (30)$	—	134
COT/ PF_3	CC	$Fe(COT)(PF_3)_3$ (trace)	—	28, 125
$Sn(allyl)_4/PF_3$	CC	$Fe(\eta^3-C_3H_5)(PF_3)_3$	$+ NO \rightarrow Fe(\eta^3-C_3H_5)(NO)(PF_3)_2$	28, 125
DMMA	CC	" $Fe(DMMA)_2$ " (10–15)	Structure unknown	140
2,5-Dimethylthiophene	CC	?	$+ CO \rightarrow Fe_2(CO)_6(C_4H_2Me_2)$	18
Hacac	CL	$Fe(acac)_2 (25)$	—	9, 140
PMe_3	CC	$HFe(CH_2PMe_2)(PMe_3)_3 (6)$	$T_{dec} = +25^\circ C$	134
	CC	$HFe(CH_2PMe_2)(PMe_3)_3 (6)$	$+ NO \rightarrow Fe(NO)_2(PMe_3)_2$	134
$P(OMe)_3$	CC	$Fe[P(OMe)_3]_3$	—	135
PF_3	CC	$Fe(PF_3)_3 (25) + Fe(PF_3)_3(\mu-PF_2)_2Fe(PF_3)_3 (25)$	—	128
$PF_3/NO/BF_3$	CC	$Fe(NO)_2(PF_3)_2 (8)$	—	84

No isolable organometallic products with $CF_3CF=CF CF_3$ (66), C_6F_6 (58), $N(allyl)_3$ (125), pyrrole (49), COT, nb, nbd (134), C_3H_8 , C_2H_4 (5a), or CO_2 (132).

b. Ru, Os

No reactions have been reported.

TABLE VII
COBALT TRIAD

Substrate	Method	Product (% yield)	Comments	References
a. Cobalt				
CO	MI	Co(CO)_n	$n = 1-4$ also $\text{Co}_2(\text{CO})_8$	37a
C_2H_4	CC, CT	$\text{Co(C}_2\text{H}_4)_3$	$T_{\text{dec}} = \text{ca. } -60^\circ\text{C}$	5a
nb	CC, CT	Co(nb)_3 (ca. 30)	$T_{\text{dec}} = -15^\circ\text{C}$	5a, 134
	CC	Co(nb)_3 (ca. 30)	+ CO $\rightarrow \text{Co}_4(\text{CO})_{12}$	134
			+ $\text{PMe}_3 \rightarrow \text{Co(nb)(PMe}_3)_3$	134
			+ $\text{P(OMe)}_3 \rightarrow \text{Co(nb)[P(OMe)}_3]_3$	134
			+ $\text{C}_3\text{H}_5\text{Br} \rightarrow [\text{Co}(\eta^3\text{-C}_3\text{H}_5)\text{Br}_2]_n$	134
$\text{C}_3\text{H}_8/\text{PF}_3$	CC	$\text{Co}(\eta^3\text{-C}_3\text{H}_5)(\text{PF}_3)_3 + \text{HCo(PF}_3)_4$	—	134
1-Butene/ PF_3	CC	$\text{Co}(\eta^3\text{-C}_3\text{H}_4\text{Me})(\text{PF}_3)_3$	—	110
1,3- $\text{C}_4\text{H}_6/\text{Me}_3\text{CH}$	CC	$\text{HCo(1,3-C}_4\text{H}_6)_2$	—	104, 110
1,4-Pentadiene	CC	$\text{HCo(1,3-pentadiene)}_2$	—	104, 110
C_5H_6	CC	$\text{Co(C}_5\text{H}_5)(\text{C}_5\text{H}_6)$ (50)	—	94, 129
			+ Isoprene $\rightarrow \text{Co(C}_5\text{H}_5)(\text{isoprene})$	110
1,5-COD	CT, RE	Co(1,5-COD)_2 (10)	$T_{\text{dec}} = -15^\circ\text{C}$	5a, 134
	RE	Co(1,5-COD)_2 (10)	+ $\text{H}_2 \rightarrow \text{Co(1,5-COD)(1,2,3-}\eta^3\text{-C}_8\text{H}_{13})$	134
			+ $\text{C}_5\text{H}_6 \rightarrow \text{Co(1,5-COD)(C}_5\text{H}_5)$	134
			+ Indene $\rightarrow \text{Co(1,5-COD)(C}_9\text{H}_7)$	134
			+ $\text{P(OMe)}_3 \rightarrow \text{Co}(\eta^3\text{-C}_8\text{H}_{13})[\text{P(OMe)}_3]_2$	134
			+ $\text{PF}_3 \rightarrow \text{Co}(\eta^3\text{-C}_8\text{H}_{13})(\text{PF}_3)_3$	134
CHT	RE	$\text{CoC}_{14}\text{H}_{15,17, \text{ and } 19}$	Inseparable mixture	133
CHT/ PF_3	CC	$\text{Co}(\eta^3\text{-C}_7\text{H}_7)(\text{PF}_3)_3$	—	133
$\text{C}_6\text{F}_5\text{Br}$	CC	$(\text{C}_6\text{F}_5\text{CoBr})_n$	Structure unknown	56
PMe_3	CC	$\text{Co(PMe}_3)_4$	—	134

TABLE VII
COBALT TRIAD

Substrate	Method	Product (% yield)	Comments	References
PF ₃	CC	Co ₂ (PF ₃) ₈ (50)	—	128
PF ₃ /NO/BF ₃	CC	Co(NO)(PF ₃) ₃ (5)	—	84
No isolable organometallic products from propene, 1-butene, 1,3- or 1,4-CHD (104, 110), 1,3-C ₄ H ₆ (1, 110), C ₆ H ₆ (65, 84), C ₆ F ₆ (65), CO ₂ (132), or COT (133).				
b. Rhodium				
CO	MI	Rh ₂ (CO) ₈	$T_{\text{dec}} = -48^{\circ}\text{C}$, also Rh(CO) ₄	37
c. Iridium				
CO	MI	Ir ₂ (CO) ₈	$T_{\text{dec}} = -58^{\circ}\text{C}$, also Ir(CO) ₄	37

TABLE VIII
NICKEL TRIAD

Substrate	Method	Product (% yield)	Comments (% yield)	References
a. Nickel				
CO	MI	Ni(CO) _n	$n = 1-4$, also Ni ₂ (CO) ₇	24, 69, 73
CO/N ₂	MI	Ni(CO) _n (N ₂) _{4-n}	$n = 1-3$	72
CO ₂	CC	Ni(CO) ₄	—	132
CS	MI	Ni(CS) _n	$n = 1-4$	91, 144
CS ₂	MI	Ni(CS ₂) _n	$n = ?$	91
C ₂ H ₄	CC, CT, MI	Ni(C ₂ H ₄) ₃	$T_{dec} = 0^{\circ}\text{C}$	5a, 48a
nb	CC, CT	Ni(nb) ₃ (53)	—	134
1,5-COD	CC, CT, RE	Ni(1,5-COD) (60)	—	5a, 109, 134
1,3-C ₄ H ₆	CC	Ni(η^3 -C ₃ H ₄ Me) ₂ (2)	$T_{dec} = 20^{\circ}\text{C}$ + 1,3-C ₄ H ₆ → NiC ₁₂ H ₁₈	109, 110 109
C ₅ H ₆	CC	Ni(C ₅ H ₅)(C ₅ H ₇) (80)	—	127
B ₉ C ₂ H ₈ Me ₂	RE	Ni(B ₉ C ₂ H ₈ Me ₂) ₂	—	134
B ₁₀ C ₂ H ₁₀ Me ₂	RE	Ni(B ₁₀ C ₂ H ₁₀ Me ₂) ₂	—	134
C ₆ F ₆	CC	(NiC ₆ F ₆) _n	Structure unknown + CO → Ni(CO) ₄ (11) + P(OMe) ₃ → Ni[P(OMe) ₃] ₄	54, 58 54, 58 54, 58
C ₆ F ₅ Cl/PEt ₃	CC	<i>trans</i> -Ni(C ₆ F ₅)Cl(PEt ₃) ₂ (32)	—	65
Sn(allyl) ₄	CC	Ni(η^3 -C ₃ H ₅) ₂	—	132
Hacac	CL	Ni(acac) ₂ (36)	—	9, 140
PF ₃	CC	Ni(PF ₃) ₄ (85)	—	128
PF ₂ H	CC	Ni(PF ₂ H) ₄	$T_{dec} = 25^{\circ}\text{C}$	121
PF ₂ Cl	CC	Ni(PF ₂ Cl) ₄ (32)	—	128
PF ₃ /PH ₃	CC	Ni(PF ₃) _n (PH ₃) _{4-n}	$n = 2-4$	128
PMe ₃	CC	Ni(PMe ₃) ₄	—	134
PPh ₃	RE	Ni(PPh ₃) ₄	Reaction in liquid paraffin at 0°C	82

No isolable organometallic products with propene (109, 110), CF₃I, MeI, EtI (54, 93), C₆H₆ (58), ClCH₂CH₂CH₂Cl (93), N(allyl)₃ (125), C₆Me₆, CHT, DBA, methylenecyclopropane, 1,4-dimethylenecyclohexane (134).

(continued)

TABLE VIII—(Continued)

Substrate	Method	Product (% yield)	Comments (% yield)	References
b. Palladium				
CO	MI	$\text{Pd}(\text{CO})_n$	$n = 1-4$	22, 44, 70, 71
CO	CT	$\text{Pd}(\text{CO})_4$	$T_{\text{dec}} = \text{ca. } -100^\circ\text{C}$	5a
C_2H_4	CC, CT	$\text{Pd}(\text{C}_2\text{H}_4)_3$	$T_{\text{dec}} = -30^\circ\text{C}$	5a, 68
nb	CC, CT	$\text{Pd}(\text{nb})_3$	$T_{\text{dec}} = +5^\circ\text{C}$	5
$\text{CF}_3\text{CF}=\text{CFCF}_3$	CC	$\text{Pd}(\text{C}_4\text{F}_8)_3$	$T_{\text{dec}} = -30^\circ\text{C}$	55, 65
	CC	$\text{Pd}(\text{C}_4\text{F}_8)_3$	+ $\text{PEt}_3 \rightarrow \text{Pd}(\text{C}_4\text{F}_8)(\text{PEt}_3)_2$ (30)	55
	CC	$\text{Pd}(\text{C}_4\text{F}_8)_3$	+ $\text{C}_5\text{H}_5\text{N} \rightarrow \text{Pd}(\text{C}_4\text{F}_8)(\text{C}_5\text{H}_5\text{N})_2$	65
$\text{CF}_3\text{CF}=\text{CFCF}_3/\text{PEt}_3$	CC	$\text{Pd}(\text{C}_4\text{F}_8)(\text{PEt}_3)_2$ (56)		55
1,5-COD	CT, RE	$\text{Pd}(1,5\text{-COD})_2$ (11)	$T_{\text{dec}} = -5^\circ\text{C}$ (pure solid)	5
	RE	$\text{Pd}(1,5\text{-COD})_2$ (11)	+ $\text{C}_2\text{H}_4 \rightarrow \text{Pd}(\text{C}_2\text{H}_4)_3$	134
			+ $\text{P}(\text{OMe})_3 \rightarrow \text{Pd}[\text{P}(\text{OMe})_3]_4$ (56)	82, 134
			+ $\text{DBA} \rightarrow \text{Pd}_2(\text{DBA})_3$	134
DBA	RE	$\text{Pd}_2(\text{DBA})_3$	Isolated as CHCl_3 adduct	134
$\text{C}_6\text{F}_5\text{Br}/\text{PEt}_3$	CC	<i>trans</i> - $\text{Pd}(\text{C}_6\text{F}_5)\text{Br}(\text{PEt}_3)_2$ (30)	—	64
$\text{CF}_3\text{Br}/\text{PEt}_3$	CC	<i>trans</i> - $\text{Pd}(\text{CF}_3)\text{Br}(\text{PEt}_3)_2$ (35)	—	64
$(\text{CF}_3\text{CO})_2\text{O}$	CC	" $\text{Pd}[\text{O}(\text{COCF}_3)_2]$ "	$T_{\text{dec}} = \text{ca. } +25^\circ\text{C}$, structure unknown	65
			+ $\text{PEt}_3 \rightarrow \text{cis-Pd}(\text{OOC}(\text{CF}_3)_2)(\text{PEt}_3)_2$	65
PMe_3	CC	$\text{Pd}(\text{PMe}_3)_4$	$T_{\text{dec}} = 20^\circ\text{C}$	134
PF_3	CC	$\text{Pd}(\text{PF}_3)_4$	$T_{\text{dec}} = -20^\circ\text{C}$	128
No isolable organometallic products with propene (107), C_6H_6 , or CHT (134).				
c. Platinum				
CO	MI	$\text{Pt}(\text{CO})_n$	$n = 1-4$	44, 69, 70
1,5-COD	CC	$\text{Pt}(1,5\text{-COD})_2$ (64)	—	107

No isolable organometallic products from propene, 1-butene or 1,3- C_4H_6 (107).

TABLE IX
INSERTION OF Ni, Pd, AND Pt ATOMS INTO CARBON-HALOGEN BONDS

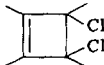
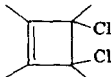
Substrate	Product (% yield)	T_{dec} (°C)	Added Ligand	Addition temp. (°C)	Product (% yield) ^a	References
a. Nickel						
CF ₃ Br	?	-78	PEt ₃	-78	CF ₃ NiBr(PEt ₃) ₂ (1)	54
C ₆ F ₅ Cl	?	-80	PEt ₃	-131	C ₆ F ₅ NiCl(PEt ₃) ₂ (10)	54
C ₆ F ₅ Br	?	-80	PEt ₃	-131	C ₆ F ₅ NiBr(PEt ₃) ₂ (10)	54
C ₃ H ₅ Cl	[Ni(η ³ -C ₃ H ₅)Cl] ₃ (75)	Stable	—	—	—	93
C ₃ H ₅ Br	[Ni(η ³ -C ₃ H ₅)Br] ₂ (60)	Stable	—	—	—	93
	[Ni(η ⁴ -C ₄ Me ₄)Cl ₂] ₂	Stable	—	—	—	133
MeCOCl	?	-100	PEt ₃	-78	NiCl ₂ (PEt ₃) ₂ (10)	54
CF ₃ COCl	?	-78	PEt ₃	-78	NiCl ₂ (PEt ₃) ₂ (20) + CF ₃ NiCl(PEt ₃) ₂	54
No isolable complexes from MeI, EtI, CF ₃ I (54), or ClCH ₂ CH ₂ CH ₂ Cl (93).						
b. Palladium						
MeBr	?	-100	PEt ₃	-131	MePdBr(PEt ₃) ₂ (trace)	54
CF ₃ Br	CF ₃ PdBr	Stable	PEt ₃	25	CF ₃ PdBr(PEt ₃) ₂ (3)	64
CF ₃ I	CF ₃ PdI	Stable	PEt ₃	25	CF ₃ PdI(PEt ₃) ₂ (10)	64
C ₂ F ₅ I	C ₂ F ₅ PdI	Stable	PEt ₃	-90	C ₂ F ₅ PdI(PEt ₃) ₂ (10) + PdI ₂ (PEt ₃) ₂ (25)	64
<i>n</i> -C ₃ F ₇ I	<i>n</i> -C ₃ F ₇ PdI	Stable	PEt ₃	25	<i>n</i> -C ₃ F ₇ PdI(PEt ₃) ₂ (9)	64
CCl ₃ Br	?	0	PEt ₃	0	PdBr ₂ (PEt ₃) ₂ (40)	64
CF ₂ Br ₂	?	-78	PEt ₃	-78	PdBr ₂ (PEt ₃) ₂ (13)	64
C ₆ H ₅ Cl	C ₆ H ₅ PdCl?	-116	PEt ₃	-116	C ₆ H ₅ PdCl(PEt ₃) ₂ (2) + PdCl ₂ (PEt ₃) ₂ (3)	54, 64

TABLE IX—(Continued)

Substrate	Product (% yield)	T_{dec} (°C)	Added Ligand	Addition temp. (°C)	Product (% yield) ^a	References
$\text{C}_6\text{H}_5\text{Br}$	$\text{C}_6\text{H}_5\text{PdBr}$	-116	PEt_3	-116	$\text{C}_6\text{H}_5\text{PdBr}(\text{PEt}_3)_2$ (11) + $\text{PdBr}_2(\text{PEt}_3)_2$ (14)	64
$\text{C}_6\text{F}_5\text{Cl}$	$\text{C}_6\text{F}_5\text{PdCl}$	Stable	PEt_3	25	$\text{C}_6\text{F}_5\text{PdCl}(\text{PEt}_3)_2$ (15)	64
			PPh_3	25	$\text{C}_6\text{F}_5\text{PdCl}(\text{PPh}_3)_2$ (7)	64
$\text{C}_6\text{F}_5\text{Br}$	$\text{C}_6\text{F}_5\text{PdBr}$	Stable	PEt_3	25	$\text{C}_6\text{F}_5\text{PdBr}(\text{PEt}_3)_2$ (8) + $\text{PdBr}_2(\text{PEt}_3)_2$ (5)	64
			PPhMe_2	25	$\text{C}_6\text{F}_5\text{PdBr}(\text{PPhMe}_2)_2$ (20) + $\text{PdBr}_2(\text{PPhMe}_2)_2$ (7)	64
			PPh_3	25	$\text{C}_6\text{F}_5\text{PdBr}(\text{PPh}_3)_2$ (8) + $\text{PdBr}_2(\text{PPh}_3)_2$ (5)	64
$\text{C}_6\text{F}_5\text{I}$	$\text{C}_6\text{F}_5\text{PdI}$	Stable	PEt_3	25	$\text{C}_6\text{F}_5\text{PdI}(\text{PEt}_3)_2$ (23)	64
$\text{C}_3\text{H}_5\text{Br}$	$[\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\text{Br}]_2$	Stable	—	—	—	55, 132
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$[\text{Pd}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}]_2$ (50)	Stable	PEt_3	25	$\text{Pd}(\sigma\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}(\text{PEt}_3)_2$	97
$\text{C}_6\text{H}_5\text{CH}(\text{CF}_3)\text{Cl}$	$[\text{Pd}(\eta^3\text{-CH}(\text{CF}_3)\text{C}_6\text{H}_5)\text{Cl}]_2$	—	—	—	—	55
$p\text{-MeC}_6\text{H}_4\text{CH}_2\text{Cl}$	$[\text{Pd}(\eta^3\text{-CH}_2\text{C}_6\text{H}_4\text{Me})\text{Cl}]_2$	—	—	—	—	55

<i>exo</i> -2-Bromonorbornene	[Pd(<i>endo</i> -norbornenyl)Br] ₂	—	—	—	55	
	[Pd(η ⁴ -C ₄ Me ₄)Cl ₂] _n	Stable	—	—	133	
MeCOCl	?	-100	PEt ₃	-78	PdCl ₂ (PEt ₃) ₂ (17)	64
Pr ⁿ COCl	?	-100	PEt ₃	0	PdCl ₂ (PEt ₃) ₂ (19)	64
CF ₃ COCl	?	-78	PEt ₃	-78	CF ₃ PdCl(PEt ₃) ₂ (4) + CF ₃ COPdCl(PEt ₃) ₂ (7) + PdCl ₂ (PEt ₃) ₂ (5)	64
<i>n</i> -C ₃ F ₇ COCl	?	-78	PEt ₃	-78	<i>n</i> -C ₃ F ₇ COPdCl(PEt ₃) ₂ (9)	64
C ₆ H ₅ COCl	?	-50	PEt ₃	40	PdCl ₂ (PEt ₃) ₂ (8)	64
C ₆ F ₅ COCl	?	-50	PEt ₃	40	C ₆ F ₅ PdCl(PEt ₃) ₂ (23)	64

No isolable complexes from MeI , EtI , CF_3Cl , or $i\text{-C}_3\text{F}_7\text{I}$ (54, 64).

c. Platinum						
$\text{C}_6\text{F}_5\text{Br}$	$\text{C}_6\text{F}_5\text{PtBr}$	Stable	PEt_3	25	<i>cis</i> - + <i>trans</i> - $\text{C}_6\text{F}_5\text{PtBr}(\text{PEt}_3)_2$	54
$\text{C}_3\text{H}_5\text{Cl}$	$[\text{Pt}(\eta^3\text{-C}_3\text{H}_5)\text{Cl}]_4$ (48)	Stable	—	—	—	104
$\text{C}_6\text{H}_5\text{CH}_2\text{Cl}$	$[\text{Pt}(\eta^3\text{-CH}_2\text{C}_6\text{H}_5)\text{Cl}]$	Stable	—	—	—	55

^a All products have *trans* configurations.

TABLE X
GROUP 1B

Substrate	Method	Product (% yield)	Comments	References
a. Copper				
CO	CT, MI	$\text{Cu}(\text{CO})_n$	$n = 1-3$, also $\text{Cu}_2(\text{CO})_6$	46, 87
C_2H_4	MI	" $\text{Cu}-\text{C}_2\text{H}_4$ "	—	52
Hacac	CL	$\text{Cu}(\text{acac})_2$ (10)	—	9, 140
No isolable organometallic complexes with C_6H_6 , C_6F_6 (58), EtBr, CH_2Cl_2 , CCl_4 (118), <i>R</i> (-)- <i>sec</i> -butyl chloride, $\text{ClCH}_2\text{CH}_2\text{Cl}$, 1,4-dibromobutane (4), $\text{PF}_3/\text{C}_3\text{H}_5\text{Cl}$, $\text{PF}_3/\text{Sn}(\text{allyl})_4$ (125), or $\text{C}_8\text{H}_5\text{Cl}$ (133).				
b. Silver				
CO	MI	$\text{Ag}(\text{CO})_n$	$n = 1-3$	46, 87
C_2H_4	MI	" $\text{Ag}-\text{C}_2\text{H}_4$ "	π -Bonded C_2H_4	52, 80a
CF_3I	CC	$\text{AgCF}_3 + \text{AgI}$	$T_{\text{dec}} = \text{ca. } -20^\circ$	56
$\text{CF}_3\text{CF}_2\text{CF}_2\text{I}$	CC	$\text{AgCF}_2\text{CF}_2\text{CF}_3(1.5) + \text{AgI}$	$T_{\text{dec}} = -20^\circ$ isolated	57
$(\text{CF}_3)_2\text{CFI}$	CC	$\text{AgCF}(\text{CF}_3)_2(5) + \text{AgI}$	Isolated as MeCN adduct	57
No isolable organometallic compound from <i>R</i> (-)- <i>sec</i> -butyl chloride (4).				
c. Gold				
CO	MI	$\text{Au}(\text{CO})_n$	$n = 1, 2$	84a
MeI	CC	?	$+ \text{Me}_2\text{S} \rightarrow (\text{Me}_2\text{AuI})_2$	131
C_2H_4	MI	$\text{Au}(\text{C}_2\text{H}_4)_n$	$n = 1, 2$	80a

TABLE XI
MAIN GROUP ELEMENTS

Substrate	Method	Product (% yield)	Comments (% yield)	References
a. Lithium				
C vapor	CC	C ₃ Li ₄ (major product)	+ H ₂ O → C ₃ H ₄ + Me ₃ SiCl → C ₃ (SiMe ₃) ₄	101 101
CO	MI	LiCO + LiOC + LiOCCO + LiCOOC + Li ₂ OCCO	—	39
CO ₂	MI	LiCO ₂ + Li ₂ CO ₂ + Li ₂ C ₂ O ₄	—	39
C ₂ H ₂	MI	LiC ₂ H ₂ + Li ₂ C ₂ H ₂	—	39
CCl ₄	CC	CLi ₄ (14)	+ C ₂ Li ₄ (61) + C ₂ Li ₂ (20) + D ₂ O → CD ₄ + C ₂ D ₄ + C ₂ D ₂ + Me ₃ SiCl → C(SiMe ₃) ₄ + C ₂ (SiMe ₃) ₄	19 19 19
C ₂ Cl ₆	CC	C ₂ Li ₆ (80)	+ D ₂ O → C ₂ D ₆ + Me ₃ SiCl → C ₂ (SiMe ₃) ₆	19 120
Haloalkanes	CC	See text	—	—
No organometallic products have been isolated with Na, K, Rb, or Cs vapors.				
b. Magnesium				
Pr ⁿ Cl	CC	Pr ⁿ MgCl (75)	—	110
Pr ⁿ I	CC	Pr ⁿ MgI (76)	—	—
			+ MeBr → MeMgBr	106
Pr ^t Br	CC	Pr ^t MgBr (55)	—	106
Bu ^t Br	CC	Bu ^t MgBr (5)	—	106
C ₆ H ₅ Cl	CC	C ₆ H ₅ MgCl (58)	—	106
CH ₂ =CHBr	CC	CH ₂ =CHMgBr (78)	—	106

Magnesium vapor does not react with neopentane (106) or 2-butyne (104). The reaction of Ca vapor with CF₃CF=CF₃, C₆F₆, C₆F₅H, C₆H₅CF₃, or fluoroalkanes (66) affords no isolable organometallic products.

(continued)

TABLE XI—(Continued)

Substrate	Method	Product (% yield)	Comments (% yield)	References
c. Zinc				
CF ₃ I	CC	"CF ₃ ZnI"	$T_{dec} = \text{ca. } -80^\circ\text{C}$, not characterized	62
Hacac	CL	Zn(acac) ₂ (28)	—	9, 140
No isolable organometallic products from CF ₃ CF=CFCF ₃ , MeI, or CF ₃ Br (62).				
d. Al, Ga, In				
CO	MI	M _n (CO) ₂	M = Al, Ga	42, 91
C ₂ H ₄	MI	"M—C ₂ H ₄ "	M = Al, Ga, In	51
Hacac	CL	Al(acac) ₃ (14)	—	10, 140
No isolable organometallic products with Al vapor from propane, propene, 1- or 2-butenes, 1,3-C ₄ H ₆ , or propyne (104, 110, 116).				
e. Silicon				
Me ₃ SiH	CC, CE	Me ₃ SiSiH ₂ SiMe ₃ (27, 14)	—	111, 112
Me ₂ SiH ₂	CE	Me ₂ SiHSiH ₂ SiHMe ₂ (30)	—	112
MeSiH ₃	CE	MeSiH ₂ SiH ₂ SiH ₂ Me (34) + <i>cyclo</i> - Me ₂ Si ₄ H ₆ (2.5)	—	112
Si ₂ H ₆	CE	Si ₅ H ₁₂	—	104
MeOH	CE	SiH ₂ (OMe) ₂ (20) + polymers	—	104
B ₂ F ₄	CE	FSi(BF ₂) ₃ (1)	—	53

Cl ₂	CE	SiCl ₄ (99) + Si ₂ Cl ₆ (trace)	—	104
HX	CE	SiH ₂ X ₂ (20–30) + polymers	X = Cl, Br	104

Silicon vapor reacts with alkanes, alkenes, alkynes, arenes, ketones, alkyl halides, and ethers to give mainly polymers (104).

f. Germanium				
CO	MI	Ge(CO) _n	—	87
CCl ₄	CC	C ₂ Cl ₆ + CCl ₃ GeCl ₃ (20)	—	80
CHCl ₃	CC	CHCl ₂ GeCl ₃ (8)	—	80
Me ₃ SiH	CC	Me ₆ Si ₂ (14) + (Me ₃ Si) ₂ GeH ₂ (3.0)	—	20
SiCl ₄	CC	SiCl ₃ GeCl ₃ (10)	—	80

Germanium vapor does not react with EtCl (80).

g. Sn, Pb				
CO	MI	Sn(CO) _n	—	87
MeI	CC	Me ₃ SnI (3.6) + Me ₂ SnI ₂ (0.4) + MeSnI ₃ (trace)	—	83
			+ EtI → Me _n Et _{3-n} SnI, n = 0–3	83
EtI	CC	Et ₃ SnI (trace) + Et ₂ SnI ₂ (3) + EtSnI ₃ (trace)	—	83
1-Iodooctane	CC	(1-Octyl) _n SnI _{4-n}	n = 1–3	83
C ₃ H ₅ Cl	CC	Sn(CH ₂ CH=CH ₂) ₃ Cl	—	83
C ₂ H ₂ /HCl	CC	Sn(CH=CH ₂) ₃ Cl (1)	—	83
Hacac	CL	M(acac) ₂	M = Sn (11), M = Pb (10)	10, 140

Tin vapor does not react with EtCl, EtBr, 1-bromohexane, 1-bromooctane, C₂H₂, propene/HCl, or Me₂S (83).

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Metal Complexes of π -Ligands Containing Organosilicon Groups

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I

INTRODUCTION

Organometallic compounds containing both organosilicon groups and transition metal atoms have received much attention in several research laboratories.

There are several ways of introducing a metal atom into an organosilicon compound, and, accordingly, the following types of compound are known: (a) metallocloxanes and siloxymetallocloxanes, including monomeric and polymeric species (8, 14, 81, 143); (b) metal silylamides (15, 23–27, 56); (c) transition metal complexes with organosilicon ligands bonded through nitrogen, phosphorus, or arsenic donor atoms (1), including aminoalkylsilane (110, 119, 124), silylketimine (144), silylnitrene (2, 60), silylphosphine and phosphinoalkylsilane (3, 4, 28, 59, 77, 146–148), and silylarsine (3, 4) complexes; (d) compounds with direct metal–silicon bonds, $M-SiR_3$ (9, 18, 39, 72, 97, 160, 170); (e) com-

pounds with σ -bonded organosilicon groups, including those with triorganosilylmethyl groups, $M-CH_2SiR_3$ (32, 40, 42, 166-168), and triorganosilylaryl groups, $M-C_6F_4SiR_3$ (64); (f) compounds with formally unsaturated organosilicon groups, π -bonded to transition metals.

The last-mentioned class (f) will be discussed in some detail in this article. Recently, the subject was briefly reviewed in a Russian booklet that is not easily obtainable (32) and was also discussed in a plenary lecture at the Fourth International Symposium on Organosilicon Chemistry (62).

II

CLASSIFICATION OF π -LIGANDS TO WHICH ORGANOSILICON GROUPS ARE σ -BONDED

The organic ligands will be classified, as is usual in transition metal organic chemistry (34), according to the number of electrons contributed by the organic ligands to the vacant metal orbitals (Fig. 1): (a) 2-electron donors (organosilyl-isocyanide, -carbene, and -olefin complexes); (b) 3-electron donors (organosilicon η^3 -allyl complexes); (c) 4-electron donors (organosilyl- η^4 -cyclobutadiene and - η^4 -silacyclopentadiene complexes); (d) 5-electron donors (organosilyl- η^5 -cyclopentadienyl complexes); (e) 6-

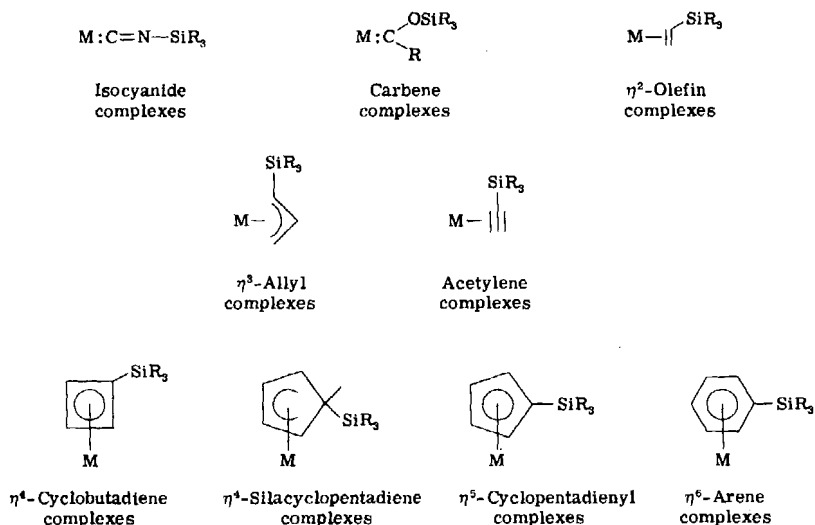


FIG. 1. Structures of some organic ligands.

electron donors (organosilyl- η^6 -arene complexes); (f) other π -ligand complexes (organosilylcycloheptatriene, -cyclooctatetraene, -pentalene, -azulene complexes); (g) compounds derived from organosilyl acetylenes.

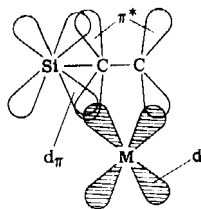
III

PARTICULAR EFFECTS OF THE σ -BONDED ORGANOSILICON GROUPS ON THE π -LIGANDS

In discussing these compounds, some legitimate questions may arise. Namely, why do organosilicon π -ligand complexes deserve special treatment compared to the other transition metal organic derivatives? Is there any particular effect or usefulness obtained by introducing a σ -bonded organosilicon group into the π -bonded organic ligand?

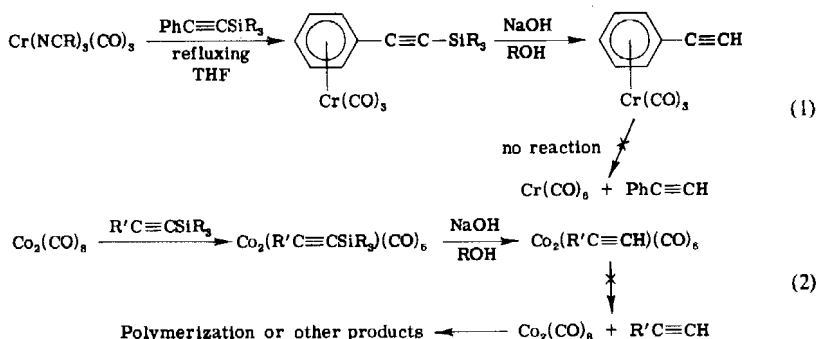
A positive answer to the second question will justify the selection of this subject for a review. Thus, the use of unsaturated organic compounds containing σ -bonded organosilicon groups as π -ligands may result in one of the following features: (a) the organosilicon moiety may act as a protecting group for a reactive site; (b) the organosilicon moiety may assist or promote some unusual reactions; (c) π -complexation may change the reactivity of the silicon-carbon bond.

In some cases, an enhanced thermal stability of silylated π -complexes relative to their silicon-free analogs has been observed (e.g., with olefins and arenes). Perhaps, the ideas advanced to explain the increased stability of silylated olefin complexes (52) are more generally applicable to other π -bonding ligands as well. Some unusual bonding may occur in silylated complexes, due to Si-C \equiv C ($d_\pi - p_\pi$) interaction, which would allow for delocalization of electron density into the silicon d orbitals, leading perhaps to enhanced backbonding from the transition metal. This might reduce electron density in the antibonding orbitals of the coordinated π -ligand, the silicon atoms thus acting as a drain for excess electron density. Such an increase in stability may be expected in all cases when backbonding from metal to the acceptor is to an antibonding orbital of the π -ligand. It may even be possible in some cases (e.g. η^2 -olefin complexes) that some direct Si-M π -interaction may occur (Fig. 2). This latter point may explain some ready migrations of SiR₃ groups from metal to ligands (see, e.g., Section III,B) that occur intramolecularly, probably with low activation energy, without necessitating formation of free SiR₃ groups in the intermediate step.

FIG. 2. Molecular orbital representation of silicon-metal π -interaction.

A. Organosilicon Moieties as Protecting Groups

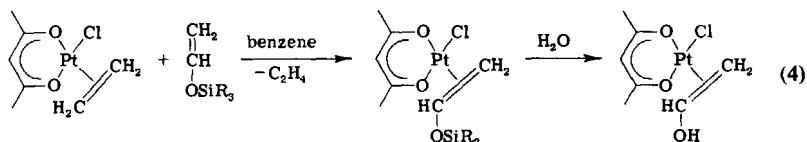
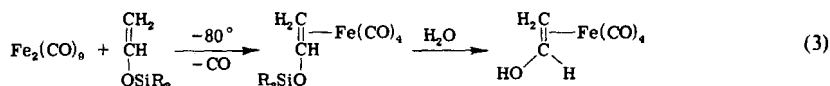
Some interesting examples illustrate the use of organosilicon groups to protect reactive sites in the synthesis of transition metal organic compounds that cannot be obtained by a direct reaction. In such procedures, an intermediate π -complex of an organosilicon ligand is first formed (and often isolated), and then the organosilicon group is eliminated by some procedure, usually hydrolytic cleavage. Thus, chromium or cobalt carbonyl complexes of monosubstituted acetylenes cannot be obtained directly, either because of lack of reaction or because of polymerization and/or secondary reactions of the ligand. This difficulty was circumvented by preparing first the π -complex of a silylated acetylene, followed by alkaline cleavage of the organosilicon groups, as shown in the following examples with chromium (45, 93) and cobalt (44) carbonyls (R = Me):



Some related reactions are cited in Section IV,C,1.

Another illustration is given by π -complexes of vinyl alcohol that cannot be prepared directly because this ligand cannot exist in the free state: it is rapidly converted into its more stable tautomer, acetaldehyde. Iron (158) and platinum (70, 157) complexes of vinyl alcohol have been

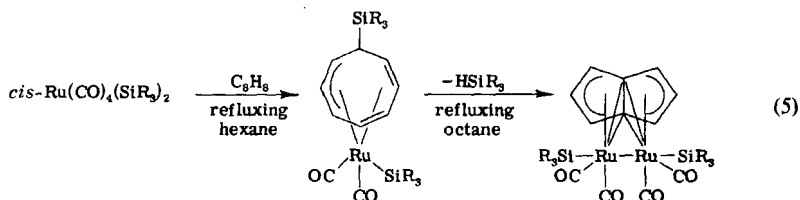
obtained, however, via organosilicon intermediates ($R = \text{Me}$):



A previous report on the preparation of $[(\text{H}_2\text{C}=\text{CH}-\text{OH})\text{PtCl}_2]_2$ via the trimethylsiloxy derivative (161) could not be confirmed (158).

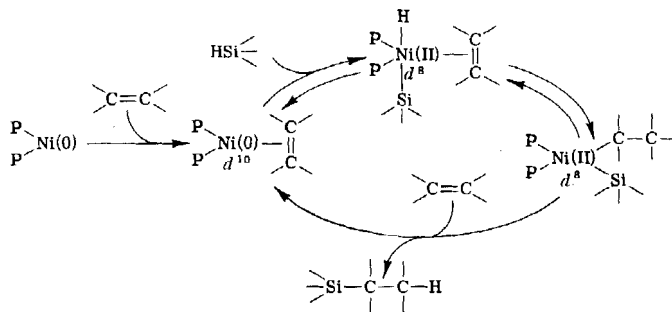
B. Unusual Reactions Assisted by Organosilicon Groups

Among the unusual reactions related to the presence of organosilicon groups in the organic ligand are those involving the migration of a trimethylsilyl group from the metal to the ligand and vice versa. An interesting example is the formation of a trimethylsilylorganoruthenium complex by SiMe_3 group migration, which undergoes dehydrogenative ring closure with loss of SiMe_3 from the ring. A new transannular C—C bond is formed and a pentalene complex ($R = \text{Me}$) is the final product (95):



Other unexpected reactions with SiR_3 group migrations will be reviewed in Section IV,F.

Migration of organosilicon groups from metal to ligand is believed to be a key step in the mechanism of olefin hydrosilylation catalyzed by nickel-phosphine complexes (89), as shown in Scheme 1. (Substituents are omitted for clarity.)



(Substituents are omitted for clarity.)

SCHEME 1

C. Changes of Si—C Bond Reactivity Caused by Metal π -Complex Formation

It is obvious that π -complex formation greatly affects the electron density in unsaturated or aromatic molecules, and this, in turn, will result in a change of Si—C bond reactivity if an organosilicon substituent is present. Two striking examples can be put forward to illustrate this point: the Si—C bond in $(\eta^6\text{-C}_6\text{H}_5\text{SiMe}_3)\text{Cr}(\text{CO})_3$ is much more readily cleaved by alcoholic alkalis than in uncomplexed $\text{C}_6\text{H}_5\text{SiMe}_3$, and the compound $(\eta^6\text{-C}_6\text{H}_5\text{CH}_2\text{SiMe}_3)\text{Cr}(\text{CO})_3$ is 3×10^5 times more reactive than uncomplexed $\text{C}_6\text{H}_5\text{CH}_2\text{SiMe}_3$ in the same type of reaction (45). It has been shown that the $\text{Cr}(\text{CO})_3$ group has a strong electron-withdrawing effect on an aromatic nucleus, similar to that of a nitro group (45). The decrease of the electron density in the ring via complex formation was confirmed by ^1H and ^{13}C NMR investigations of several substituted arylchromium tricarbonyl complexes, including trimethylsilyl derivatives (48, 115, 125).

It has also been mentioned in the literature that bis(trimethylsilylbenzene)chromium, $\text{Cr}(\eta^6\text{-C}_6\text{H}_5\text{SiMe}_3)_2$, undergoes rapid Si—C bond cleavage in absolute methanol at room temperature, in contrast to the inertness of the uncomplexed trimethylsilylbenzene in methanol (47).

The effect of π -complexation varies with the nature of the transition metal, in as yet an unpredictable manner. Thus, in the acidolytic Si—C bond cleavage of trimethylsilylmetallocenes $(\eta^5\text{-C}_5\text{H}_5)\text{M}(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)$ ($\text{M} = \text{Fe}, \text{Ru}, \text{Os}$) leading to formation of unsilylated metallocenes, the reactivity varies according to the following order of rate constants: $\text{Ru} > \text{Os} > \text{Fe}$ (111). The reactivity of trimethylsilylruthenocene is said to be ca. 45 times greater than that of trimethylsilylferrocene (111).

Ready cleavage of Si—C bonds was observed in reactions of allyltrimethylsilane with Pd(II) and Hg(II) compounds (92, 133, 169), and of alkynyltrimethylsilanes with Pt(II) complexes (126). Probably, in all cases π -complex formation occurs as an intermediate step, and this promotes Si—C bond cleavage.

It is quite surprising that the influence of π -complex formation on the reactivity of Si—C bonds has been so little investigated to date, in spite of the importance of such studies for the purpose of regulating the chemical behavior of organosilicon compounds.

IV

TYPES OF π -LIGAND COMPLEX CONTAINING ORGANOSILICON GROUPS

A. Two-Electron Donors

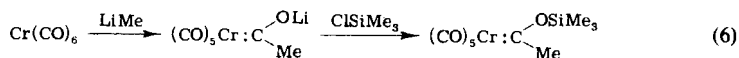
1. Organosilyl Isocyanide Complexes

Direct reaction of iron pentacarbonyl with trimethylsilyl isocyanide ($\text{:C}\equiv\text{N}-\text{SiMe}_3$) at $65^\circ\text{--}75^\circ$ yields an air-sensitive substitution product $\text{Me}_3\text{Si}-\text{N}\equiv\text{C}:\text{Fe}(\text{CO})_4$ in 93% yield, with elimination of carbon monoxide (152). It was shown by infrared spectroscopy (38) that complex formation lowers the $\text{N}\equiv\text{C}$ bond order for $\text{Me}_3\text{Si}-\text{N}\equiv\text{C}:$, whereas it raises the $\text{N}\equiv\text{C}$ bond order for $\text{Me}_3\text{C}-\text{N}\equiv\text{C}:$, presumably as a result of interaction between d_π orbitals of silicon with the metal d orbitals.

A less conventional preparation of isocyanide complexes involves the reaction of iron pentacarbonyl with metalated (sodium or lithium derivative) hexamethyldisilazane (162).

2. Organosilicon Carbene Complexes

Treatment of chromium hexacarbonyl with methyllithium, followed by addition of chlorotrimethylsilane, gave a silylated carbene complex (114), which decomposed above 40° :



The siloxy derivative is more reactive than the methoxy analog in substitution reactions with ammonia and amines (114).

Another organosilicon carbene complex is formed by treating chro-

mium hexacarbonyl with trimethylsilylmethylolithium in the presence of tetramethylammonium bromide (35), to give $(\text{CO})_5\text{Cr}:\text{C}(\text{CH}_2\text{SiMe}_3)\text{O}^-\text{NMe}_4^+$. The Si—C bond in this complex is also readily cleaved by several reagents (ammonia, alcohols).

3. Organosilicon Olefin Complexes

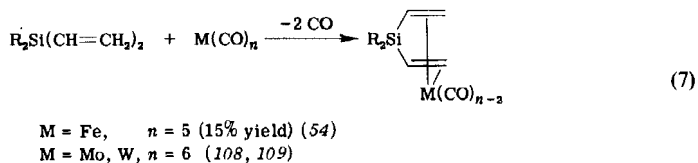
Very few such compounds are known. Three general procedures can be used for their preparation: (a) addition of the olefin to a transition metal compound; (b) replacement of carbon monoxide in metal carbonyls; and (c) migration of organosilicon groups from metal to ligand in some reactions of silylmetal compounds with acetylenes.

Copper(I) chloride complexes have been obtained by direct addition of the organosilicon olefin [e.g., $\text{R}_3\text{Si}-\text{CH}=\text{CH}_2$ or $\text{R}_2\text{Si}(\text{CH}=\text{CH}_2)_2$] at -78° to copper(I) chloride; the yields of these complexes vary from 40% for $\text{Me}_3\text{Si}-\text{CH}=\text{CH}_2\cdot\text{CuCl}$ to 80% for $\text{Me}_2\text{Si}(\text{CH}=\text{CH}_2)_2\cdot 2\text{CuCl}$ (52, 55). The silylated vinyl copper(I) complexes are more stable than the unsubstituted ones. Thus $\text{Me}_3\text{Si}-\text{CH}=\text{CH}_2\cdot\text{CuCl}$ decomposes at 120° (but is unstable *in vacuo*), whereas the ethylene complex of CuCl is unstable at room temperature. Moreover, $\text{Me}_2\text{Si}(\text{CH}=\text{CH}_2)_2\cdot 2\text{CuCl}$ (decomposition temperature 100°) is stable to extended pumping at room temperature (52). An explanation was suggested in Section II.

Olefin exchange has been used for the preparation of certain platinum(II) complexes (67). Thus, trimethylvinylsilane replaces ethylene in Zeise's salt to give the compound $\text{K}[\text{Cl}_3\text{Pt}(\text{H}_2\text{C}=\text{CHSiMe}_3)]$. The SiMe_3 group in this complex is readily cleaved by water (wet acetone) with elimination of hexamethyldisiloxane and regeneration of Zeise's salt, but resists attack by pyridine *N*-oxide, which instead replaces a chlorine atom (67).

A similar exchange was reported for *p*-trimethylsilylstyrene (105), which in the reaction with Zeise's salt yields $\text{K}[\text{Cl}_3\text{Pt}(\text{CH}_2=\text{CH}-\text{C}_6\text{H}_4\text{SiMe}_3-p)]$, with liberation of ethylene.

Elimination of carbon monoxide from metal carbonyls and coordination of the organosilicon olefin has been reported for divinylsilanes (54, 108, 109) (the compounds obtained are air-sensitive):

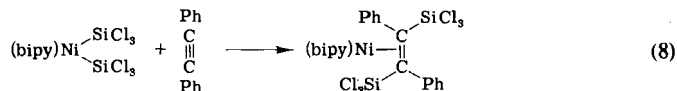


Similarly, tetravinylsilane reacts with Group VI metal carbonyls to give $\text{Si}(\text{CH}=\text{CH}_2)_4[\text{M}(\text{CO})_4]_2$ ($\text{M} = \text{Mo, W}$) (88), but the reaction of

$\text{Si}(\text{CH}=\text{CH}_2)_4$ with dicobalt octacarbonyl yielded the cluster compound $\text{H}_2\text{C}=\text{CH}-\text{SiCo}_3(\text{CO})_9$ (87).

The reaction of $\text{Me}_2\text{Si}(\text{CH}=\text{CH}_2)_2\text{Fe}(\text{CO})_3$ with triphenylphosphine resulted in displacement of the olefin rather than carbon monoxide, with formation of $\text{Fe}(\text{CO})_3(\text{PPh}_3)_2$, thus showing a weaker coordination of dimethyldivinylsilane (54).

A less orthodox formation of a silylated olefin complex was observed in the reaction of $(\text{bipy})\text{Ni}(\text{SiCl}_3)_2$ with acetylenes (90, 91):



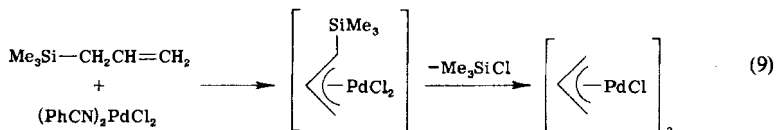
The air-sensitive violet complex thus formed was treated with methylmagnesium bromide and then hydrolyzed to give *trans*- $\text{Ph}(\text{Me}_3\text{Si})\text{C}=\text{CPh}(\text{SiMe}_3)$ (90, 91). Apparently, this is the first example of transfer of silyl groups from a metal to a coordinated hydrocarbon ligand. It seems that a similar step is involved in the "dehydrogenative *cis* double silylation" of acetylenes catalyzed by diethyl(bipyridyl)nickel(II) (156).

Several attempts to prepare palladium(II)-olefin complexes have failed. Thus, organosilicon groups from β -trimethylsilylstyrene were cleaved (as chlorotrimethylsilane) by palladium(II) chloride (164) with formation of *trans,trans*-1,4-diphenyl-1,3-butadiene.

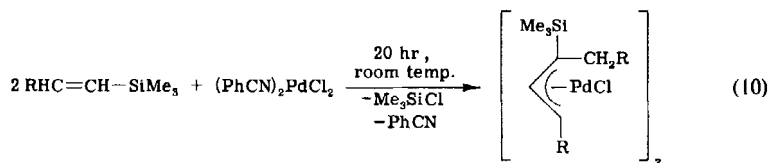
B. Three-Electron Donors

In some early attempts, the formation of η^3 -allylic complexes containing organosilicon groups was not successful. Thus, the reaction of allyltrimethylsilane with Zeise's salt occurred with olefin exchange to give an η^2 -complex, $\text{K}[\text{Cl}_3\text{Pt}(\text{H}_2\text{C}=\text{CH}-\text{CH}_2\text{SiMe}_3)]$ (53).

The reaction of allyltrimethylsilane with bis(benzonitrile)palladium dichloride gave an η^3 -allylic complex, but with elimination of the organosilicon group (169). Cleavage of silicon-allyl bonds in $\text{Me}_3\text{Si}-\text{CH}_2\text{CH}=\text{CH}_2$ also occurs with lithium tetrachloropalladate, lithium diacetatodichloropalladium(II), and palladium(II) acetate in methanol or hydrolytic media (92), and with mercury(II) salts (133). Probably π -complex formation, which activates the Si-C bond toward cleavage (see Section III,C), occurs as an intermediate step:



The formation of some silylated η^3 -allylic complexes has been, however, achieved by reacting substituted silyl olefins with bis(benzonitrile)palladium dichloride. The mechanism is rather complex and two olefin molecules are incorporated in the final η^3 -allylic ligand (169):

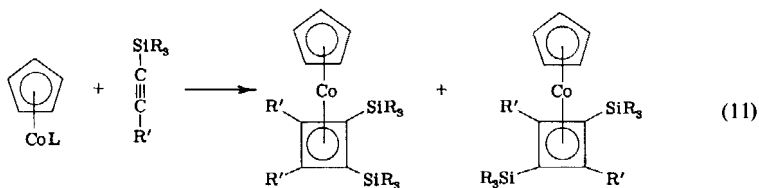


In this reaction, SiR_3 groups are only partially eliminated.

C. Four-Electron Donors

1. Silylated Cyclobutadiene Complexes

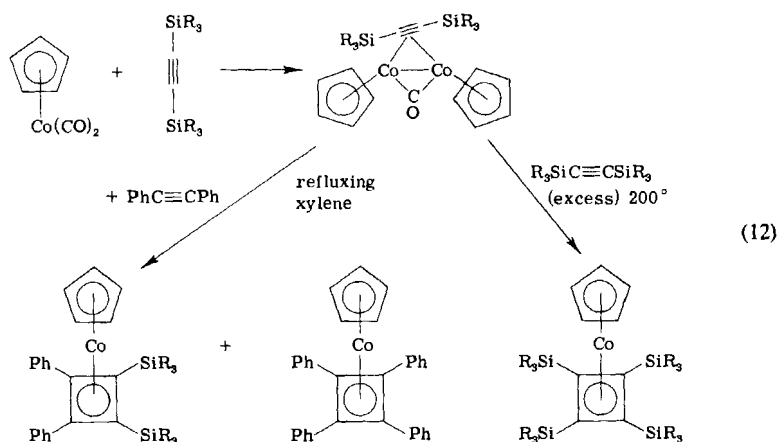
These compounds have been obtained indirectly by reactions of silylated acetylenes with metal carbonyls or olefin complexes. Thus, trimethylsilylphenylacetylene reacts with η^5 -cyclopentadienylcobalt dicarbonyl, cobaltocene, or η^5 -cyclopentadienyl-(1,3-cyclooctadiene) cobalt, in refluxing xylene, to give a mixture of *cis*- and *trans*-bis-(trimethylsilyl)cyclobutadiene complexes ($\text{R} = \text{Me}$, $\text{R}' = \text{Ph}$) (68, 127, 137):



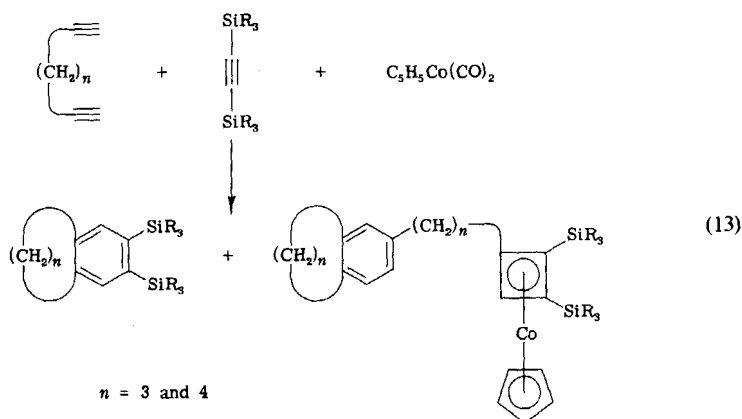
Trimethylsilyl groups in these compounds are cleaved with hydrochloric acid giving the first cobalt-cyclobutadiene complexes with unsubstituted positions in the four-membered ring. The protecting role of SiMe_3 groups (see also Section III, A) is important here, since phenylacetylene does not give cyclobutadiene complexes under similar conditions, but trimerizes instead.

The structures of the silylated cyclobutadiene complexes were established by mass spectrometry and X-ray diffraction studies (13, 85, 127). It was found that the planes of the two rings are almost parallel.

Bis(trimethylsilyl)acetylene reacts with η^5 -cyclopentadienyldicarbonylcobalt to give a stable bridged acetylene complex, which can further react with diphenylacetylene (in refluxing xylene) or with bis(trimethylsilyl)acetylene (at 200° in autoclave) (137, 139) to give silylated η^4 -cyclobutadiene complexes [Eq. (12) (R = Me)]. The tetrakis(trimethylsilyl)cyclobutadiene complex is formed in only 4.7% yield. It can be also obtained (in only 1.2% yield) by heating cobaltocene with bis(trimethylsilyl)acetylene at 180° for 43 hr (139).

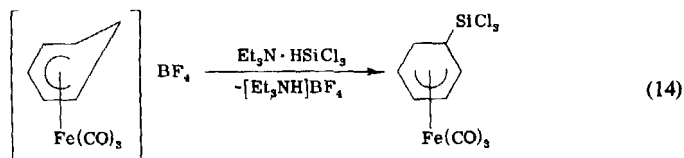


A silylated cyclobutadiene complex of unusual structure was formed, along with silylated bicyclic compounds, in the reaction of terminal alkydiynes with bis(trimethylsilyl)acetylene and cyclopentadienyldicarbonylcobalt in refluxing octane (R = Me) (69):



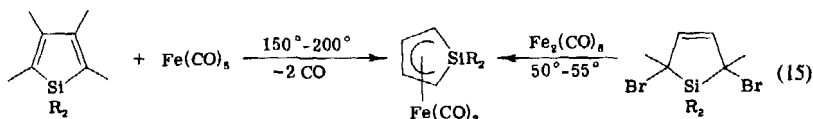
2. Silylated Cyclohexadiene Complexes

The only known example of this type of compound is a η^4 -trichlorosilylcyclohexadienetricarbonyliron complex, prepared (89% yield) by the reaction of cyclohexadienyltricarbonyliron tetrafluoroborate with trichlorosilane-triethylamine adduct in acetonitrile at 40° (117):

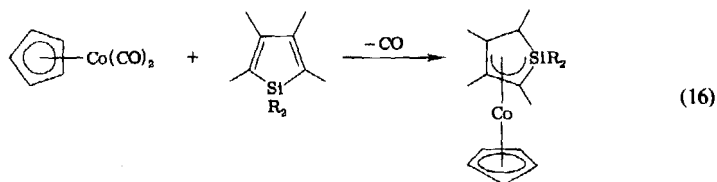


3. Silacyclopentadiene Complexes

Various substituted silacyclopentadienes react with iron or cobalt carbonyl compounds to give stable η^4 -silacyclopentadiene complexes. Thus, with iron pentacarbonyl, reaction occurs at 150°–200° in an autoclave, with $\text{Fe}_2(\text{CO})_9$ at 40°–60°, and with $\text{Fe}_3(\text{CO})_{12}$ at 80° (20, 21, 49, 132); the same complex can be obtained from a dibromosilacyclopentene and diiron nonacarbonyl, under mild conditions (19):



In a similar manner, silacyclopentadienes react with cyclopentadienylcobalt dicarbonyl to give an η^4 -complex (49, 138):

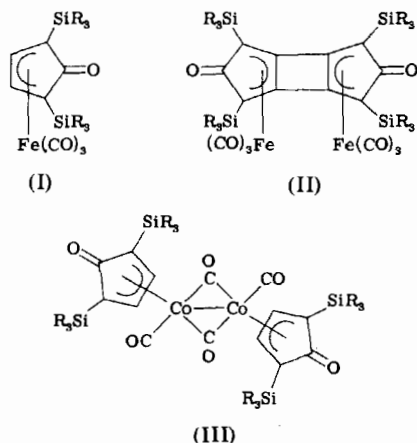


The silicon heteroatom does not seem to participate in the conjugation and the butadiene fragment is not perturbed, thus allowing formation of η^4 -complexes.

Attempts to form silacyclopentadienyliron complexes by reactions of Si-chlorosilacyclopentadienes with anions such as $\text{C}_5\text{H}_5\text{Fe(CO)}_2^-$, $\text{C}_5\text{H}_5\text{Mo(CO)}_3^-$, Mn(CO)_4^- , and Co(CO)_4^- failed (41).

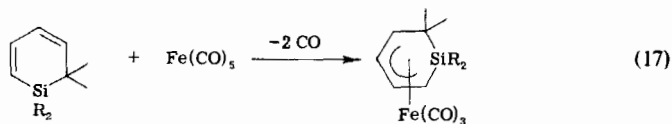
4. Silylated Cyclopentadienone Complexes

Some of the products formed in reactions of certain acetylenes with metal carbonyls are η^4 -cyclopentadienone complexes. Among those reported are some organosilicon derivatives. Thus, trimethylsilylacetylene reacted with dodecacarbonyltriiron at 60° – 100° to give $[(\text{Me}_3\text{Si})_2\text{R}_2\text{C}_5\text{O}]\text{Fe}(\text{CO})_3$ ($\text{R} = \text{H}$ or Ph), believed to have structure I (78, 165). A related complex (II), containing two cyclopentadienone ring systems and, therefore, two iron atoms, was obtained from 1,4-bis(trimethylsilyl)butadiyne and dodecacarbonyltriiron (123). A dinuclear cobalt complex (III) was obtained from $(\text{Me}_3\text{Si}-\text{C}\equiv\text{C}-\text{SiMe}_3)\text{Co}_2(\text{CO})_6$ and trimethylsilylacetylene ($\text{R} = \text{Me}$), and also by heating $\text{Hg}[\text{Co}(\text{CO})_4]_2$ with trimethylsilylacetylene at 90° (100). None of these structures has been confirmed by X-ray diffraction studies, and the exact position of the trimethylsilyl groups is not known.



5. Silacyclohexadiene Complexes

Silacyclohexadienes may, in principle, act as 4-electron donors. Indeed, 1,1-dimethyl-1-silacyclohexa-2,4-diene reacts with iron pentacarbonyl to give a complex in which the diene fragment is bonded to iron (50):



If the ring carries four phenyl substituents (in positions 2, 3, 4, and 5),

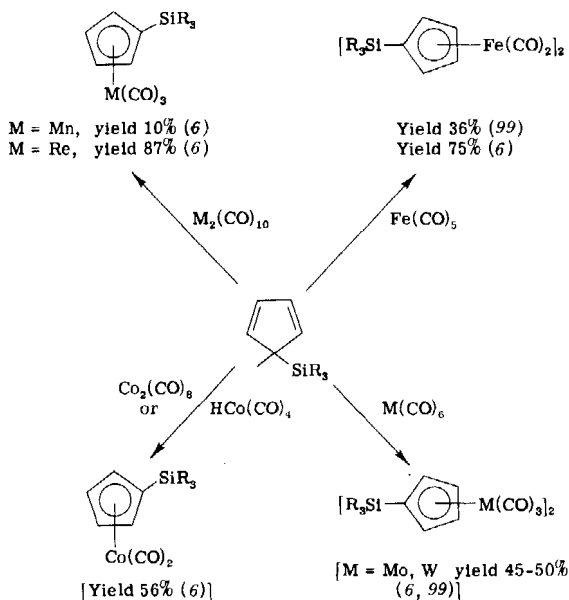
iron pentacarbonyl causes isomerization (to a 1-silacyclohexa-2,5-diene) and no complex is formed (50).

D. Five-Electron Donors

1. Silylated Cyclopentadienyl Complexes

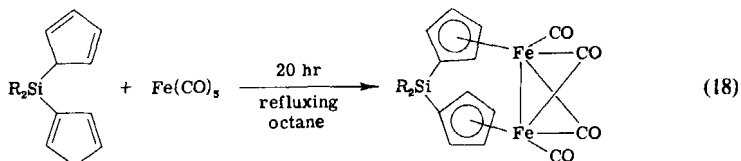
Organosilyl substituted η^5 -cyclopentadienyl complexes may be prepared by two main procedures: (a) reactions of silylated cyclopentadienes or their alkali metal derivatives, with an appropriate transition metal compound (carbonyl or halide) with formation of π -bonds; (b) metalation of a preformed η^5 -cyclopentadienyl complex, followed by treatment with an organohalosilane.

Triorganosilylcyclopentadienes react on heating with various metal carbonyls (in a manner similar to unsubstituted cyclopentadiene) to give triorganosilylcyclopentadienylmetal carbonyls, in satisfactory-to-good yields, as shown by the examples (5, 6, 99, 129, 136) in Scheme 2. No SiR_3 cleavage [except some with $\text{Mn}_2(\text{CO})_{10}$] or insertion into the $\text{Si}-\text{C}_5\text{H}_5$ bond was observed in any of these reactions. The structure of $\eta^5-(\text{Me}_3\text{Si}-\text{C}_5\text{H}_4)\text{Re}(\text{CO})_3$ has been confirmed by X-ray diffraction analysis (66).



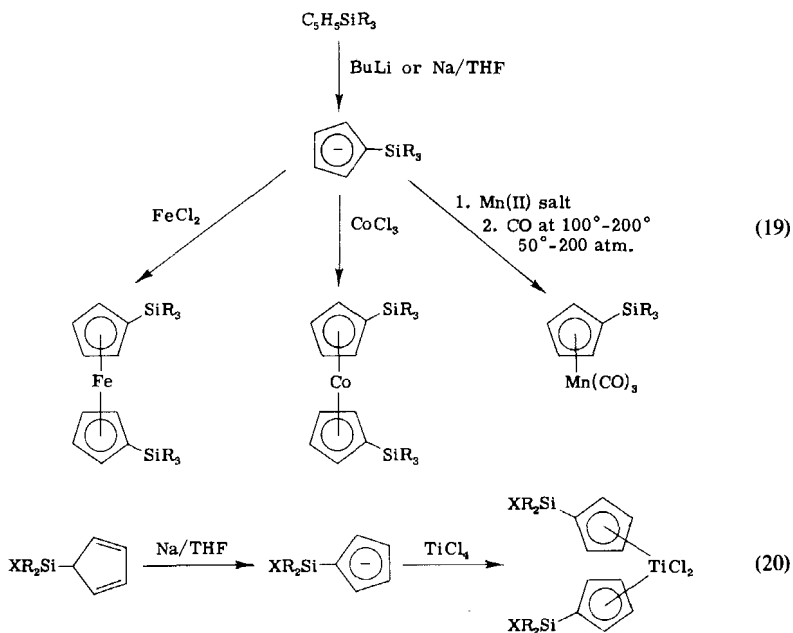
SCHEME 2

An interesting compound is formed in the reaction of dimethyl-bis(cyclopentadienyl)silane with iron pentacarbonyl, in refluxing octane [its structure was confirmed by X-ray diffraction (163)]:



The two C_5H_5 rings in this molecule have a cis-eclipsed configuration (163).

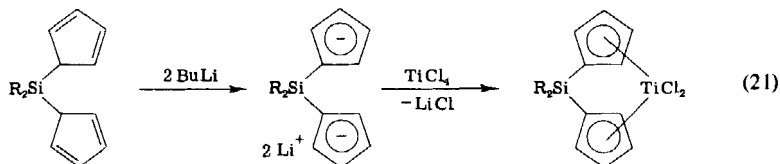
Several preparations of silylated cyclopentadienylmetal complexes involve the formation of a triorganosilylcyclopentadienyl anion (by treatment of a silylated cyclopentadiene with an alkali metal in tetrahydrofuran or by metalation with *n*-butyllithium), followed by reaction with metal chlorides. This type of reaction has been used for the synthesis of silylated ferrocenes (41, 43, 58, 83, 84, 103, 107, 116, 135, 142, 171, 172), cobaltocenes (135), nickelocene (135), titanium cyclopentadienyls (46, 145), and cyclopentadienylmanganese tricarbonyl (30) [Eqs. (19) and (20)]. It is remarkable that $\text{Si}-\text{C}_5\text{H}_5$ bonds are not



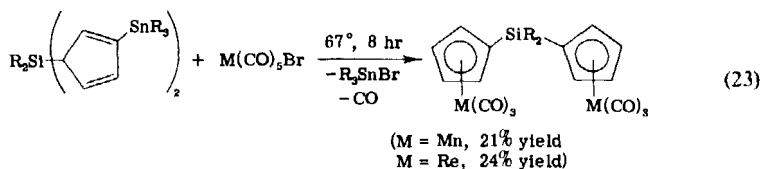
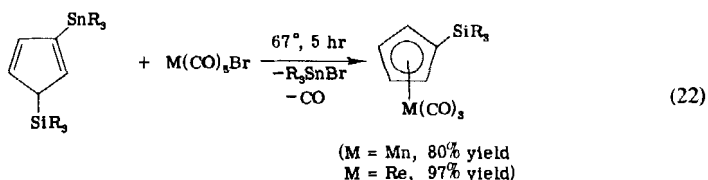
SCHEME 3

cleaved by either the alkali metals or the alkyllithiums used. By using this procedure, silylated ferrocenes have been prepared containing the following groups: SiMe_2OEt (140), $\text{SiMe}_2(\text{OSiMe}_2)_n\text{R}$ (140, 141, 142), $\text{SiMe}_2\text{CH}_2\text{Cl}$ (141), $\text{SiMe}_2\text{C}_5\text{H}_5$ (135), CH_2SiR_3 (104), $\text{SiMe}_2\text{SiMe}_3$ (101, 103).

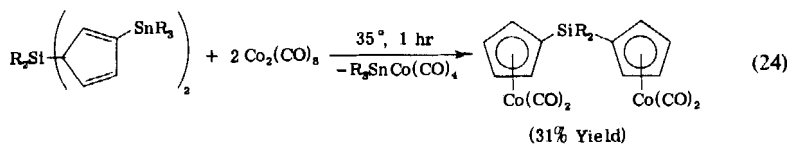
Dialkylbis(cyclopentadienyl)silanes can be used in a similar manner, as in the following preparation of a titanium derivative ($\text{R} = \text{Me}$) (96):



A very versatile preparation seems to be the elimination of organotin halides in the reaction of organostannyl-organosilylcyclopentadienes with metal carbonyl halides. This reaction is very selective and only $\text{Sn}-\text{C}$ bonds are cleaved with formation of η^5 -cyclopentadienyl complexes (7):

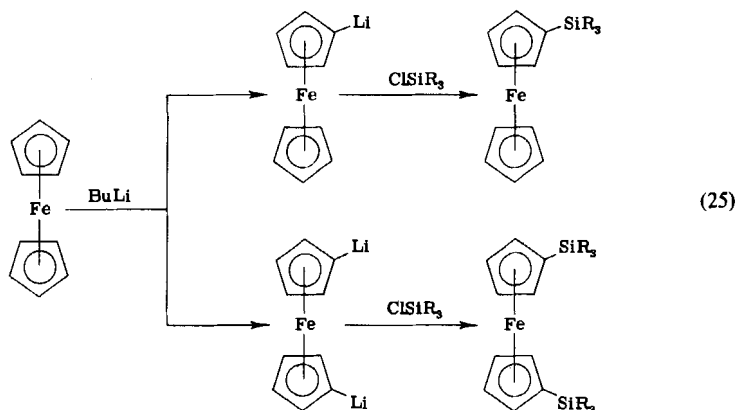


The reaction was also used for the synthesis of compounds containing $\text{SiMe}_2\text{SiMe}_3$ and CH_2SiMe_3 groups in the cyclopentadienyl ring (7). In a similar manner, triorganotin groups are eliminated in reactions with dicobalt octacarbonyl, with formation of η^5 -complexes (7):



Several preparations involve the metalation of a preformed η^5 -cyclo-

pentadienyl complex, followed by treatment with an organochlorosilane. One of the first examples involved ferrocene (10, 11, 57, 58, 131), which may be metalated with *n*-butyllithium in either one or two cyclopentadienyl rings:

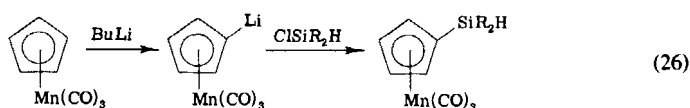


The reaction has been extended to ruthenocene and osmocene (111) and has been used extensively in ferrocene chemistry, e.g., for introducing groups such as $\text{SiMe}_2\text{SiMe}_3$ (98, 102, 103), $\text{SiMe}_2\text{CH}_2\text{SiMe}_3$ (104), SiMe_2Cl (130), trans-annular $\text{SiMe}_2\text{CH}_2\text{SiMe}_3$ (104), $\text{SiMe}_2\text{C}_6\text{H}_4\text{R}$ (159), SiHRR' (116), and for the preparation of tetraferrocenylsilane (134). Ferrocenylsodium can also be used (12, 149), but with no advantage over ferrocenyllithium. The reaction of ferrocenyllithium with optically active organochlorosilanes was found to be highly stereospecific (29).

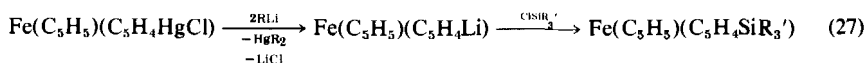
Ferrocene can be polyolithiated, by treatment with several equivalents of *n*-butyllithium in hexane–benzene solvent at 100° or in the presence of a chelating tertiary diamine (TMED). Addition of trimethylchlorosilane to the product so obtained affords a mixture containing $\text{FeC}_{10}\text{H}_{10-n}(\text{SiMe}_3)_n$ ($n = 1-7$) compounds. The tetrakis derivative ($n = 4$) was isolated as a pure substance; other members of the series were identified only by gas chromatography and mass spectrometry (65).

The chemistry of silylated ferrocenes is rather extensive and will not be discussed here in detail. We only mention the cleavage of SiMe_3 groups from $\text{Fe}(\text{C}_5\text{H}_4\text{SiMe}_3)_2$ by mercury(II) chloride to give $\text{Fe}(\text{C}_5\text{H}_4\text{SiMe}_3)(\text{C}_5\text{H}_4\text{HgCl})$ (112) and some interesting reactions at silicon in the side chain of ferrocene derivatives (86, 130). The structure of $\text{Fe}(\text{C}_5\text{H}_4\text{SiMe}_2\text{SiMe}_3)_2$ has been established by X-ray diffraction analysis (71).

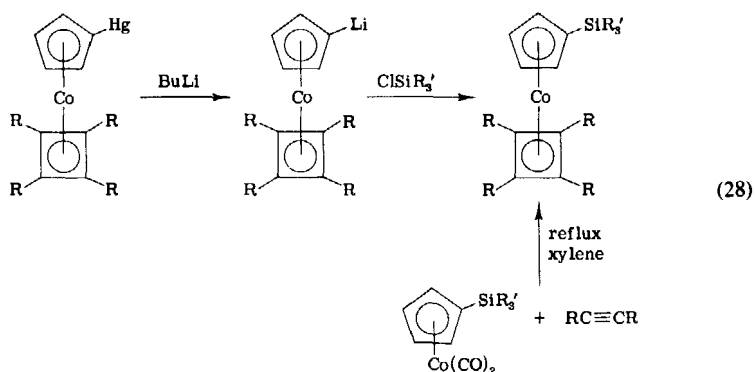
Cyclopentadienyltricarbonylmanganese can also be metalated with *n*-butyllithium and then converted into organosilicon derivatives (33, 61):



An alternative method for preparing metallocenyllithium derivatives, convertible into organosilicon compounds, is based on cleavage of organomercury compounds with organolithium reagents. It was used for the silylation of ferrocene (113, 151):

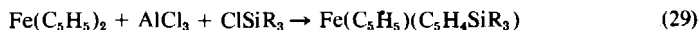


The method has the advantage that it ensures formation of pure monosubstituted ferrocene, free of the disilylated products. This procedure has been used also for lithiation of a cyclopentadienylcobalt derivative, which showed ferrocene-like behavior ($R = \text{Ph}$) (128, 129):



The silylated product exhibits an interesting ^1H NMR spectrum in that the resonance of the SiMe_3 protons occurs at higher fields ($\tau = 10.2$ ppm) than in the ferrocene analogs.

Direct silylation of ferrocene, without the intermediacy of an organo-metallic compound, has been achieved under Friedel-Crafts conditions, with chloro- and aminosilanes (154):

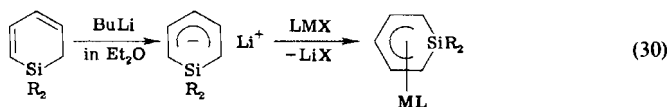


Although this reaction provides a facile route to silylated ferrocenes, its scope has not been fully investigated.

2. Silacyclohexadienyl Complexes

A very interesting potential 5-electron donor ligand is the recently prepared stable silacyclohexadienyl anion, which is formed by metala-

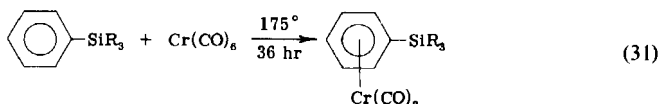
tion of dimethylsilacyclohexadiene with *n*-butyllithium (31). It can be anticipated that this anion will show a cyclopentadienyl-type behavior and, therefore, a new class of silacyclohexadienylmetal complex can be expected:



E. Six-Electron Donors

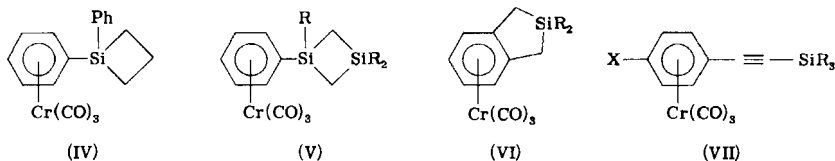
1. Silylated π -Arene Complexes

Aromatic organosilicon compounds react with chromium hexacarbonyl on prolonged heating to give the corresponding silylated η^6 -arene chromium tricarbonyl complexes (51, 150). The trimethylsilyl derivative, obtained in 20% yield, is air-stable as a solid:



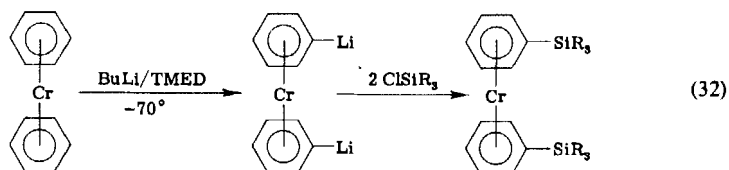
Compound (*p*-Me₃SiC₆H₄SiMe₃)Cr(CO)₃, in 70% yield, was similarly prepared by using (CH₃CN)₃Cr(CO)₃ as the starting material (82). A recent improvement of this reaction involved using Cr(NH₃)₃(CO)₃ as the starting material, which allows the reaction to be carried out in refluxing dioxane (115). With polyphenylsilanes, only one aromatic group was found to react with chromium hexacarbonyl (106).

Some novel silicon-containing arene–chromium tricarbonyl complexes (IV–VII), derived from phenyl-substituted silacyclobutanes (118), 1,1-dimethylsilaindane (120) and alkynylarenes (45), have been prepared by essentially identical methods. It is worth mentioning here that the organosilicon complex (VI) is somewhat more thermally stable than the silicon-free 1,1-dimethylindane complex (120).



The ¹H and ¹³C NMR spectra of (η^6 -C₆H₅SiMe₃)Cr(CO)₃ have been analyzed in detail and compared with those of other arene–chromium tricarbonyl complexes (48, 125).

A second synthetic procedure for preparing silylated arene complexes, based on the metalation of a preformed η^6 -arene complex, followed by treatment with an organochlorosilane, has been used only in one case so far; namely, bis(benzene)chromium (47):



The compound is very air-sensitive and forms a yellow cation on oxidation (47).

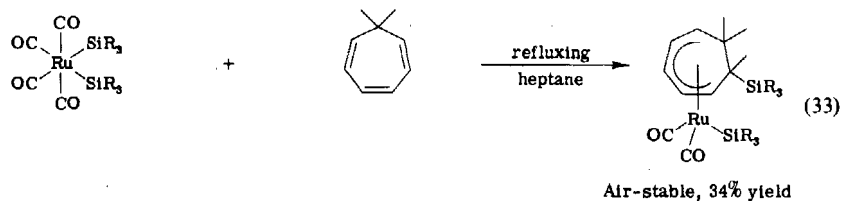
A Grignard reagent ($\eta^6\text{-C}_6\text{H}_5\text{MgI}$)Cr(CO)₃ gave only an 8% yield of ($\eta^6\text{-C}_6\text{H}_5\text{SiMe}_3$)Cr(CO)₃ with chlorotrimethylsilane (82).

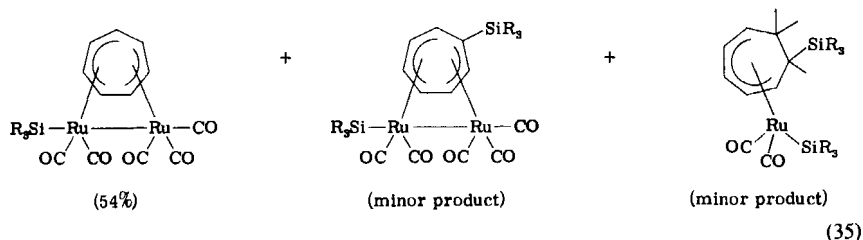
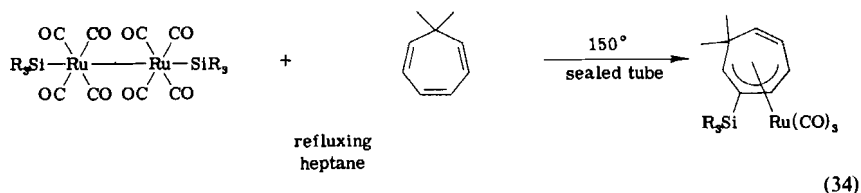
F. Large Ring and Bicyclic Ligand Complexes

Large ring polyenes (e.g., cycloheptatriene or cyclooctatetraene) are able to form metal π -complexes, but in many cases they do not act as 7- or 8-electron donors to one metal atom; rather they tend to form polynuclear complexes, formally donating sets of 3 or 4 electrons to a metal cluster. Alternatively, they only partially use their ring π -electrons in bonding to a single metal atom. In several cases, the large ring undergoes some transannular cyclization to form complexes of a bicyclic ligand.

1. Silylated Cycloheptatriene Complexes

Some interesting reactions have recently been found to occur on heating cycloheptatriene with some organosiliconruthenium carbonyls. An unexpected feature of these reactions is the migration of trimethylsilyl groups from the metal to the π -ligand (R = Me) (17, 74):



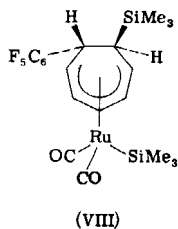


The SiR_3 group migration seems to be an intramolecular process, since practically no crossover products were formed in the reaction of a mixture of $\text{Ru}(\text{CO})_4(\text{SiMe}_3)_2$ and $\text{Ru}(\text{CO})_4(\text{GeMe}_3)_2$ with cycloheptatriene (17).

The X-ray structure determination on $(\text{Me}_3\text{SiC}_7\text{H}_6)\text{Ru}_2(\text{CO})_5(\text{SiMe}_3)$ confirmed the presence of one SiMe_3 group as a ligand substituent and the $\eta^3 - \eta^4$ bonding of the two metal atoms (16, 76). The $\text{OC}-\text{Ru}-\text{Ru}$ sequence is almost linear, but the terminal SiMe_3 group is bent away (173°).

The migration of SiR_3 groups from $\text{Ru}(\text{CO})_4(\text{SiR}_3)_2$ ($\text{R} = \text{Me}$) to the π -ligand, seems to be a rather general reaction, since it was found to occur also with substituted cycloheptatrienes ($7\text{-R}'\text{C}_7\text{H}_7$, where $\text{R}' = \text{Me}, \text{Ph}, \text{C}_6\text{F}_5$) (16, 17). By contrast, the reactions of $[\text{Ru}(\text{CO})_4\text{SiMe}_3]_2$ with $7\text{-R}'\text{C}_7\text{H}_7$ [where $\text{R}' = \text{CN}$ and O^tBu] afford the parent complex $\text{C}_7\text{H}_7\text{Ru}_2(\text{CO})_5(\text{SiMe}_3)$, presumably via loss of $\text{SiMe}_3\text{R}'$ (16).

The X-ray structure determination of $(\text{Me}_3\text{Si})(\text{C}_6\text{F}_5\text{C}_7\text{H}_7)\text{Ru}(\text{CO})_2(\text{SiMe}_3)$ (VIII) reveals unexpectedly that the SiMe_3 substituent on

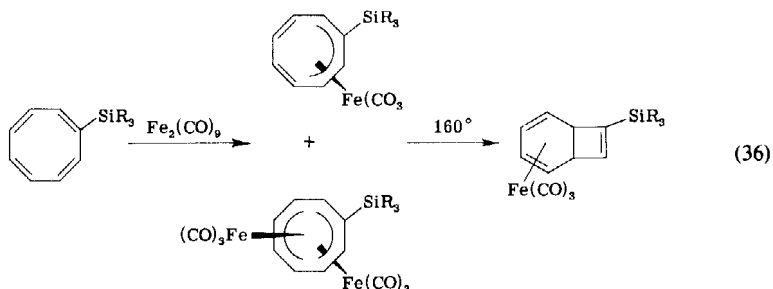


the seven-membered ring is in an *anti* position (74). It is interesting to mention here that there is no similarity in the behavior of cyclohepta-

triene and cyclopentadiene on reaction with $\text{Ru}(\text{CO})_4(\text{SiMe}_3)_2$. Cyclopentadiene forms $(\eta^5\text{-C}_5\text{H}_5)\text{Ru}(\text{CO})_2\text{SiMe}_3$, with elimination of a trimethylsilyl group as HSiMe_3 , without any migration from metal to ligand (155).

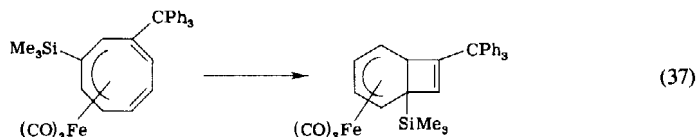
2. Complexes of Silylated Cyclooctatetraenes

Heating trimethylsilylcyclooctatetraene with diiron nonacarbonyl yields both mono- and bis(irontricarbonyl) derivatives. Further heating of the monoiron derivative at 160° in a sealed tube results in transannular cyclization, to give the bicyclic isomer (36, 37):



For the diiron compound, infrared spectra showed that the two $\text{Fe}(\text{CO})_3$ groups are on opposite sides of the ring, rather than forming a $\text{Fe}_2(\text{CO})_6$ cluster with an Fe-Fe bond (37).

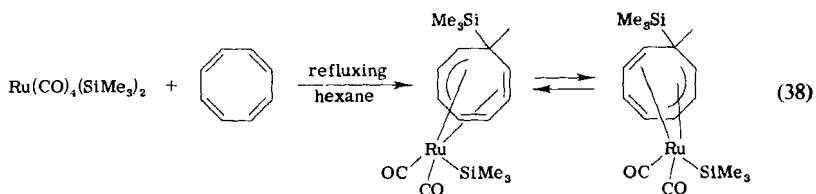
Treatment of $(\eta^4\text{-C}_8\text{H}_7\text{SiMe}_3)\text{Fe}(\text{CO})_3$ with $\text{Ph}_3\text{C}^+\text{BF}_4^-$ in nitromethane gives a tetrafluoroborate salt, which on hydrolysis yields a triphenylmethyl-substituted derivative, $(\text{Me}_3\text{Si})(\text{Ph}_3\text{C})\text{C}_8\text{H}_6\text{Fe}(\text{CO})_3$ (37). Proton magnetic resonance spectra suggested that the $\text{Fe}(\text{CO})_3$ group is coordinated to the SiMe_3 -carrying diene system (37). The triphenylmethyl derivative undergoes transannular cyclization, and the position of SiMe_3 and CPh_3 groups in the product was established by X-ray diffraction (36):



It was shown that in this compound the six-membered ring is folded into two planar segments (with a dihedral angle of 142°); the iron atom is bonded to a delocalized diene fragment (36).

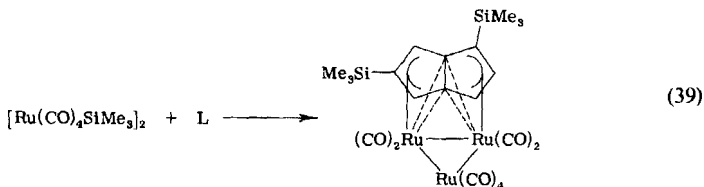
Bis(trimethylsilyl)ruthenium tetracarbonyl reacts with cyclooctatetraene in refluxing hexane, to give silylated π -complexes, formed by

migration of the silyl group from the metal to the organic group (95):

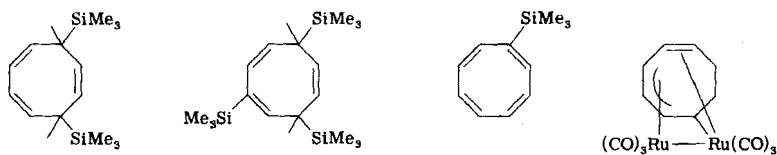


3. Silylated Pentalene Complexes

The pentalene ring system is difficult to prepare by the conventional procedures of organic synthesis, and until very recently it was almost unknown (95). Therefore, the recent discovery that silylated pentalene complexes are readily formed by some transannular cyclizations of eight-membered rings was an elegant synthesis of this bicyclic system. Thus trimethylsilyl-substituted cyclooctatrienes and -tetraenes, as well as the cyclooctadienyl complex $\text{C}_8\text{H}_{10}\text{Ru}_2(\text{CO})_6$, react with the dinuclear ruthenium complex $[\text{Ru}(\text{CO})_4\text{SiMe}_3]_2$ to give the same triruthenium octacarbonyl complex of a disilylated pentalene in 10–30% yields (75, 95):



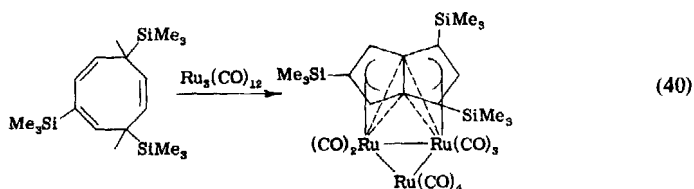
Here L represents one of the following eight-membered ring compounds:



Migration of SiMe_3 groups from metal to ligand occurs in those cases in which the parent compounds contain less than two organosilyl groups in the eight-membered ring. However, when the starting material is a tris(trimethylsilyl)cyclooctatriene, one of the organosilyl groups is lost from the ligand.

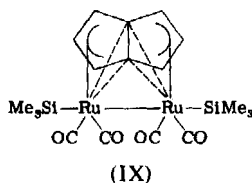
The structure of the pentalene complex was confirmed by X-ray diffraction (75). The compound in Eq. (39) is not fluxional (95).

A tris(trimethylsilyl)pentalene complex was obtained in 15% yield from a trisubstituted cyclooctatriene with $\text{Ru}_3(\text{CO})_{12}$ (75, 95):



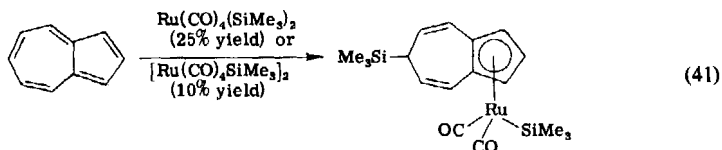
The tris(trimethylsilyl) complex exhibits fluxional behavior (75).

The mechanism of these dehydrogenative ring closures that yields pentalene complexes is still unclear. In some reactions, the SiR_3 groups seems to play no role, as illustrated by the formation of pentalenes containing the $\text{Ru}_3(\text{CO})_8$ fragment from either $\text{Ru}_3(\text{CO})_{12}$ or $[\text{Ru}(\text{CO})_4\text{SiMe}_3]_2$. However, the formation of the pentalene complex (IX) from cyclooctatetraene and *cis*- $\text{Ru}(\text{CO})_4(\text{SiMe}_3)_2$ (see Section III,B) involves a crucial migration of SiMe_3 groups, with formation of a silylated cyclooctatrienyl complex as intermediate (95).

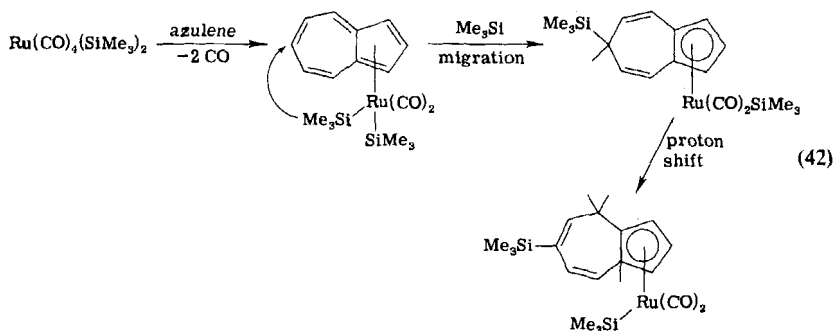


4. Complexes of Silylated Azulenes

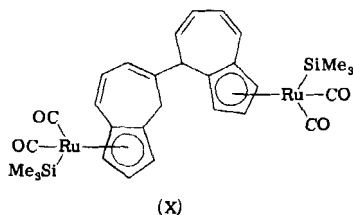
In the reactions of azulene with trimethylsilylruthenium carbonyl complexes in refluxing heptane, there occurs a migration of organosilicon groups from metal to ligand to give complexes of silylated azulenes (94):



The mechanism of this reaction is thought to involve the following steps (94):



In the reaction of azulene with $[\text{Ru}(\text{CO})_4\text{SiMe}_3]_2$, two other products were isolated, namely $\text{Ru}_2(\text{CO})_2(\text{C}_{10}\text{H}_8)$ (10% yield) and $\text{Ru}_2(\text{SiMe}_3)_2(\text{CO})_4(\text{C}_{10}\text{H}_8)$ (5% yield). The probable structure of the diruthenium compound (94) is



Structure X has yet to be demonstrated by X-ray diffraction methods.

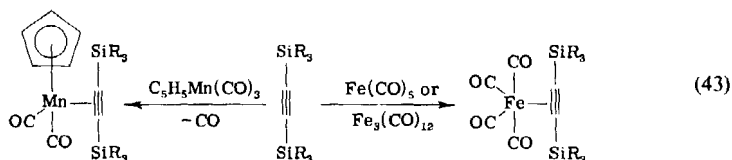
G. Complexes of Silylated Acetylenes

Acetylenes are discussed separately here because, in reactions with transition metal compounds, they can act in a variety of ways (34). Thus, they can act as monodentate (2-electron donors) or as bridging groups (4-electron donors), or they can undergo chemical transformations to form cyclobutadiene, cyclopentadienone, or other moieties that incorporate the parent acetylene as a part of the cyclic π -ligand. Some examples of this last type have already been mentioned (Sections IV, C, 1 and 4).

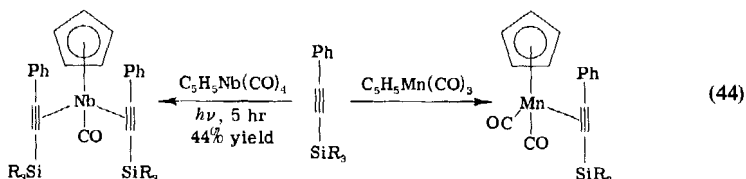
1. Acetylenes as Monodentate Ligands

Bis(trimethylsilyl)acetylene reacts with iron pentacarbonyl or with triiron dodecacarbonyl (73, 123) and with cyclopentadienylmanganese

tricarbonyl (123) by replacing carbon monoxide to form η^2 -complexes (R = Me):



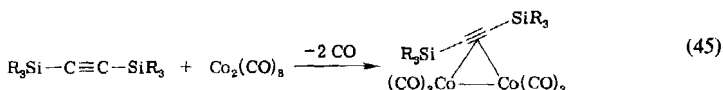
In a similar manner, UV irradiation of (triphenylsilyl)phenylacetylene with cyclopentadienylmanganese tricarbonyl (121) and cyclopentadienyl-niobium tetracarbonyl (122) results in elimination of carbon monoxide and formation of monodentate acetylene complexes (R = Ph):



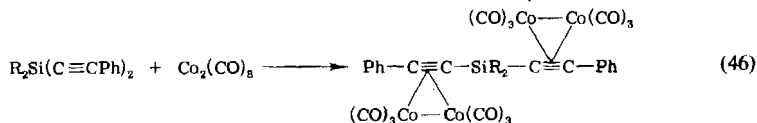
Platinum(II) halides in ethanol cleave trimethylsilylalkynyls, without isolation of a complex (126). Possibly π -complex formation occurs as an intermediate step.

2. Acetylenes as Bridging Ligands

Bis(trimethylsilyl)acetylene and some other monosilylated acetylenes react with dicobalt octacarbonyl to form dinuclear complexes with bridging acetylenes, similar to those formed by other acetylenes (100, 123, 153):



In a similar manner, dimethyl-bis(phenylethynyl)silane forms a derivative in which both acetylenic groups act as bridging ligands (79, 80):

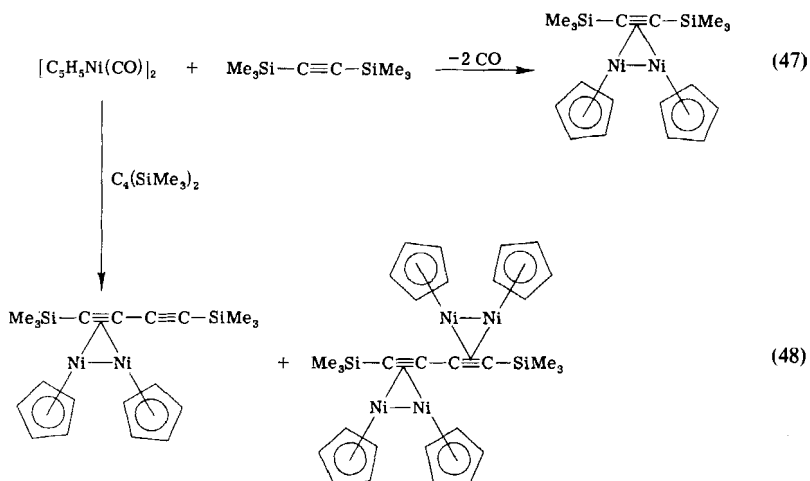


Chromium hexacarbonyl, dimanganese decacarbonyl, and $[\text{C}_5\text{H}_5\text{Fe}(\text{CO})_2]_2$ gave no isolable complexes with $\text{R}_2\text{Si}(\text{C}\equiv\text{CPh})_2$ (80).

1,4-Bis(trimethylsilyl)butadiyne forms, on reaction with dicobalt octa-

carbonyl, compounds in which one or two acetylenic groups are coordinated (123).

Cyclopentadienylnickel carbonyl dimer is also known to react with acetylenes to form bridged complexes. With bis(trimethylsilyl)acetylene and with 1,4-bis(trimethylsilyl)butadiyne it reacts to give organosilyl acetylene complexes (63) [Eqs. (47) and (48)]. The silylated butadiyne



complexes would be interesting precursors for the presently unknown complexes of unsubstituted butadiyne if desilylation of the complex could be achieved; preliminary experiments have failed (63).

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NOTE ADDED IN PROOF

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Activation of Alkanes by Transition Metal Compounds

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I

INTRODUCTION

In 1968, at a Faraday Society Discussion on Homogeneous Catalysis, Jack Halpern said that "the development of successful approaches to the activation of carbon-hydrogen bonds, particularly in saturated hydrocarbons, remains to be achieved and presently constitutes one of the most important and challenging problems in this whole field" (39). On thermodynamic grounds the cleavage of the C—H bond, by reaction with a transition metal complex, is expected to be about as favorable as the cleavage of the H—H bond. However, although in 1968 there were many examples of hydrogen activation, there was only one example (8) of a C—H bond in an alkyl group being activated by a transition metal.

The first step in the transition metal-catalyzed reaction of an organic compound is an electronic exchange that corresponds to an acid-base interaction between the inorganic catalyst and organic substrate; com-

pounds that are catalysts can be conveniently divided, using Pearson's nomenclature (77, 78) into *hard* and *soft* (99). A hard catalyst is one of Pearson's "hard" acids; if it is a metal ion it will generally be in a high oxidation state and its catalytic properties will be directly related to its low polarizability and high polarizing power. These hard catalysts undergo 1-electron oxidation reductions, and free radicals are formed as intermediates from the organic substrates (39, 89). Such reactions are also called *homolytic* as there is homolytic splitting of the C—H bond (i.e., $\text{C—H} \rightarrow \text{C}\cdot + \cdot\text{H}$). The compounds usually involved are soluble metal salts (e.g., acetates and naphthenates) of the early members of transition metal Groups VI to VIII (i.e., Cr, Mn, Fe, Co, and Ni), and whether or not catalysis will occur will depend on the ease of electron transfer from the substrate to the metal, i.e., on the redox potential.

A soft catalyst is one of Pearson's "soft" acids; if it is a compound of a metal it will be a complex of one of the later members of Group VIII (i.e., Ru, Os, Rh, Ir, Pd, or Pt), usually in a low oxidation state. These soft catalysts undergo 2-electron oxidation reductions, and the substrate reacts while coordinated to the metal. Such reactions are also called *heterolytic*, as there is heterolytic splitting of the C—H bond [$\text{C—H} \rightarrow \text{C}^{\cdot-} + \text{H}^+$ (or $\text{C}^+ + \text{:H}^-$)].

Alkanes can be activated by both hard and soft transition metal complexes. Hard catalysts have been known for a long time, although examples involving alkanes are few in number, and all are from studies of recent years. Soft catalysts have become important and have been much studied during the past decade and are widely used for reactions of unsaturated hydrocarbons. It was the use of such soft catalysts that Halpern had particularly in mind when he spoke of the development to activate alkanes as an important and challenging problem.

Why did he think this was so? One answer is that alkanes are available as raw material for the chemical industry, and new reactions by which they can be converted into functionally substituted organic compounds are likely to be of considerable interest to the industrial chemist. A second answer is that the nature of any interaction between an alkane and a transition metal must be quite different from that of other hydrocarbons (i.e., alkenes, alkynes, and aromatic compounds) having π -electrons that can play a dominant role.

In an alkane, all the carbon atoms have hydrogen attached to them, i.e., for a particular arrangement of carbon atoms the alkane is the fully reduced form. Reactions of alkanes that do not involve cleavage of the carbon chain, are, therefore, necessarily oxidations. An important exception, which is particularly relevant here, is hydrogen–deuterium exchange. In one sense this is a "nonreaction" in that the alkane is both the reactant and the product.

The reactions discussed here are mainly those in which activation is by soft transition metals. The catalysis of alkane oxidation by hard catalysts is confined to Section IV,B. The topics discussed divide into four groups. The first is the activation of C—H bonds in ligands—these are usually phosphines, and the reactions are *stoichiometric*. The second group is that of *catalysis* of hydrogen–deuterium exchange; and the third group is the reactions of alkanes involving transition metal compounds. For groups two and three, the reactions parallel very closely reactions of aromatic compounds, and we use the results of studies on aromatic compounds where appropriate to illuminate the work on alkanes. The review is concluded with a small collection of miscellaneous topics that do not conveniently fit into the earlier sections.

It is pertinent to comment here on what is omitted. Much work has been done on, and there is much current interest in, the oxidation of hydrocarbons by oxygen. The homogeneous catalysis of such reactions by metal complexes has been comprehensively reviewed by Sheldon and Kochi (89). Such studies show that, if the reactivity is enhanced by a transition metal salt, it may be because the alkane interacts with the transition metal [and such reactions are of interest here (see Section IV,B)], or, more often, it is because an oxygen-containing species is activated, for example, the metal ion generates free radicals by decomposition of hydroperoxide radicals. Such reactions are not included in this review. This restriction means that the very interesting areas of biochemical oxidation of alkanes (81, 90) and chemical modelling on biochemical systems (67, 71, 90) are omitted, since both of these areas involve oxygen activation, the reactions being via free radicals or by the “oxenoid” mechanism (40). [See Mimoun and Seree de Roch (67) for a typical reaction scheme.]

II

ACTIVATION OF C—H BONDS IN LIGANDS

Evidence of the activation of C—H bonds in ligands by the transition metal to which the ligand is attached has come from three sources.

1. Intramolecular ring-closure reactions of phosphine ligands. Here compounds are formed when a C—H bond in the phosphine undergoes oxidative addition to the metal to form a chelate ring containing a metal–carbon bond. The hydrogen that is initially attached to the carbon is expelled as a proton together with a negative ion that is initially attached to the transition metal.

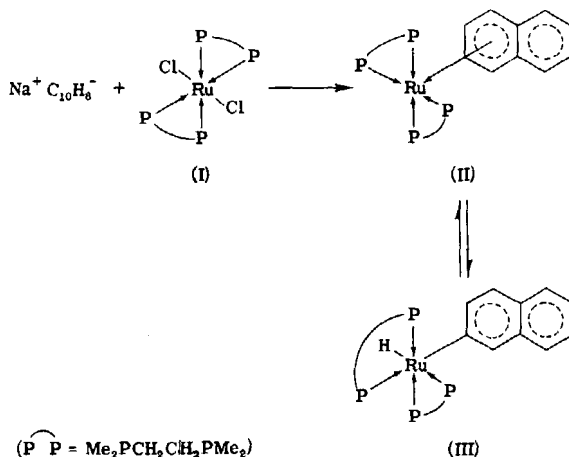
2. Hydrogen–deuterium exchange in phosphine ligands. Here hydrogen in the phosphine is exchanged for deuterium that is either in the

solvent or introduced as deuterium gas by a reaction that involves intermediates formed as in reactions type 1.

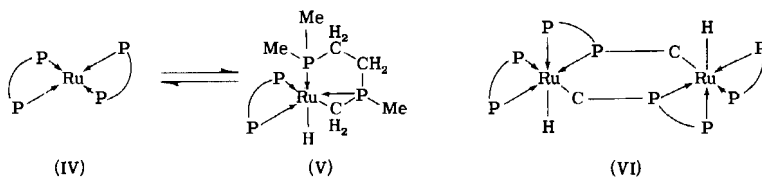
3. Compounds with hydrogen in a ligand coordinated to a transition metal. Here the hydrogen in the ligand occupies one of the coordination sites around the metal.

A. Intramolecular Ring-Closure Reactions of Phosphine Ligands

The first reported interaction between a C—H bond in a ligand and a soluble transition metal complex was that reported by Chatt and Davidson (8). The reaction product from the reaction of sodium naphthalene with *trans*-dichlorodi-(dmpe)ruthenium(II) (I) (dmpe = 1,2-bisdimethylphosphinoethane) was found to be a tautomeric equilibrium mixture of the ruthenium(0) complex (II) that contains a π -complexed naphthalene ligand and the ruthenium(II)-hydrido complex (III) where a C(2)—H bond has added to the ruthenium:

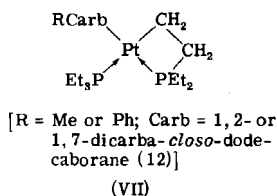


In the solid state, the equilibrium is in favor of the hydrido complex (III), and its crystal structure and that of the osmium(II) analog have been determined (38). Chatt also observed that, on heating the equilibrium mixture of (II) and (III), naphthalene was eliminated and the product $\text{Ru}(\text{dmpe})_2$ was also a tautomeric mixture. Here the tautomerism involves breaking and re-formation of carbon-hydrogen bonds in the methyl groups of the phosphine ligands (IV and V):



This then was the first report of a compound in which alkyl C—H bond activation by a transition metal had occurred. In the solid state, this equilibrium is also in favor of the hydrido complex (V), and its crystal structure has recently been determined (15). It shows compound V to be a dimer (VI), the oxidative addition of the methyl group of a ligand on each ruthenium atom being to a second ruthenium atom. Presumably one reason why this occurs is because the product of intramolecular ring closure would contain a highly strained three-membered Ru—P—C ring (i.e., in monomer V).

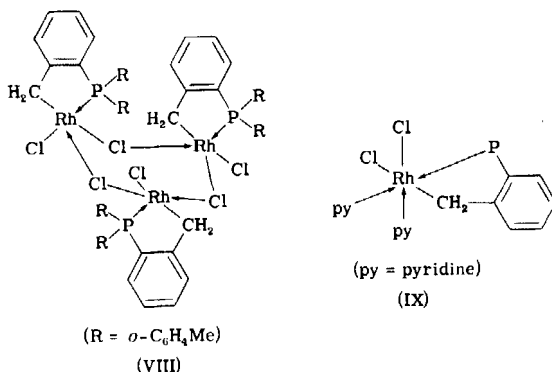
When *trans*-PtCl₂(PEt₃)₂ reacts with the lithium derivatives of carboranes (alkyl- or aryl-monosubstituted 1,2-dicarba-*closo*-dodecaborane(12) or its 1,7-isomer) the compounds formed contain two phosphine groups and one carborane (7). But analytical, molecular weight, conductivity, spectroscopic, and magnetic measurements all indicate that the compounds are four-coordination complexes of platinum(II). It does not appear possible to attain four-coordination by interaction with the alkyl or aryl group on the carborane, and the complexes are thought to have structure VII in which hydrogen is lost, as HCl, from one of the ethyl



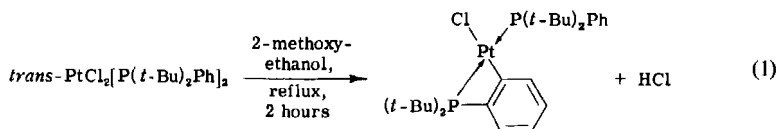
groups on the phosphine and a four-membered Pt—P—C—C ring is formed.

Intramolecular ring closures in a transition metal complex where a C—H bond of an aromatic ring is involved are well known [e.g., Parshall (75)], and during an investigation of the effect of a sterically hindered phosphine, tri-*o*-tolylphosphine, on the chemistry of rhodium-phosphine complexes, Bennett and Longstaff (4) observed a ring closure that occurred by loss of hydrogen from a methyl group of the tolylphosphine. Rhodium(III) chloride and tri-*o*-tolylphosphine were heated together in 2-methoxyethanol and a trimeric complex, [RhCl₂{P(*o*-C₆H₄Me)₂(C₆H₄CH₂)}]₃, was formed. The favored structure for this

complex is that containing a six-membered ring of alternate rhodium and chlorine atoms (VIII). Compound VIII reacts with a variety of reagents; the crystal structure of the product of the reaction with pyridine (Compound IX) has been determined (63) and fully confirms that a five-membered Rh—P—C—C—C ring is present.

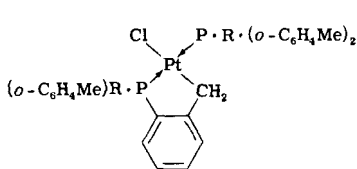


The effect of having bulky groups (e.g., *t*-butyl) in the phosphine ligand of platinum and palladium complexes has been studied in some detail by Shaw and his co-workers (9-12, 30, 31, 88). They have used a number of phosphines containing aromatic groups, e.g., di-*t*-butylphenylphosphine; intramolecular ring closure occurs with the elimination of HCl (9, 10), e.g.,

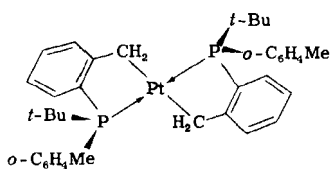


Steric effects appear to be very important in causing such ring closures; if the complex used has dimethylphenylphosphine in place of di-*t*-butylphenylphosphine as the ligand, then a reaction such as Eq. (1) does not occur.

The influence of other groups in the phosphine on the reactivity of the methyl group in the *o*-tolyl ligand has also been studied (9-12). When $\text{trans-PtCl}_2[\text{P}(o\text{-C}_6\text{H}_4\text{Me})_2\text{Ph}]_2$ is heated in 2-methoxyethanol solution, complex X, (R = Ph) containing a five-membered chelate ring is formed, but if the complex with the phosphine containing only one *o*-tolyl group and two small methyl groups is used [i.e., if it is $\text{PMe}_2(o\text{-C}_6\text{H}_4\text{Me})$], then ring closure does not take place (10). Ring closure occurs very readily in both platinum and palladium complexes if the *o*-tolylphosphine also contains bulky *t*-butyl groups (3, 11). When Na_2PtCl_4 and $\text{P}(t\text{-Bu})(o\text{-C}_6\text{H}_4\text{Me})$

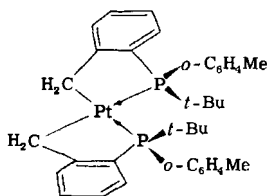


(X)

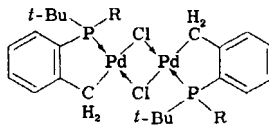
(R = Ph or *t*-Bu)

(XI)

$\text{C}_6\text{H}_4\text{Me})_2$ are heated together under reflux in *n*-propanol, ring-closure product X (R = *t*-Bu) is obtained. When this compound is heated in 2-methoxyethanol for 90 minutes, ring closure of the second phosphine ligand takes place to give the *trans* isomer (XI). The *cis*-analog (XII) can also be prepared by heating compound X (R = *t*-Bu) in decalin at 190°C for 6 days. The phosphine containing two *t*-butyl groups is less reactive, but ring closure products analogous to compound X can be obtained by heating the phosphine with *trans*- $\text{PtCl}_2(\text{PhCN})_2$ in *n*-propanol.



(XII)



(XIII)

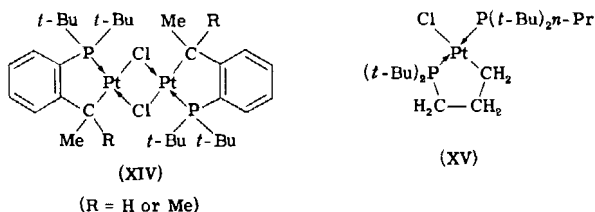
(R = *t*-Bu or *o*- $\text{C}_6\text{H}_4\text{Me}$)

Dimeric palladium complexes (XIII; R = *t*-Bu or *o*- $\text{C}_6\text{H}_4\text{Me}$) are also readily formed by heating Na_2PdCl_4 with either of the phosphines, in appropriate solvents (12). Similar complexes of platinum, but not of palladium, can be prepared from the arsine analogs, $\text{As}(t\text{-Bu})(o\text{-C}_6\text{H}_4\text{Me})_2$ and $\text{As}(t\text{-Bu})_2(o\text{-C}_6\text{H}_4\text{Me})$ (88). Slightly more rigorous conditions are required to form the arsine complexes than are required for the phosphine analogs.

Five-membered ring products are usually more stable than those containing four- or six-membered rings. This is shown when the phosphine with an ethyl or isopropyl group in the ortho position of the benzene ring is used in place of the *o*-tolylphosphine (30, 31). When $\text{P}(t\text{-Bu})_2o\text{-EtPh}$ is heated with *trans*- $\text{PtCl}_2(\text{PhCN})_2$ in *n*-propanol solution, the chlorine-bridged binuclear product (XIV; R = H), containing the five-membered ring formed by ring closure at the secondary carbon atom of the ethyl group, is formed. The palladium analog of complex

XIV ($R = H$) can also be prepared. If $P(t\text{-Bu})_2O\text{-isopropylphenyl}$ is the phosphine used, then ring closure occurs at the tertiary carbon atom to give, again, a five-membered ring product (XIV; $R = \text{Me}$).

Intramolecular ring formation is also found to occur by reaction of the C—H bond of an alkyl group attached directly to the phosphorus. For example, if $\text{trans-PtCl}_2[P(t\text{-Bu})_2n\text{-Pr}]_2$ is heated in 2-methoxyethanol solution, the product is thought to be the complex with a five-membered chelate ring (XV) formed by reaction of the terminal methyl of the n -propyl group.



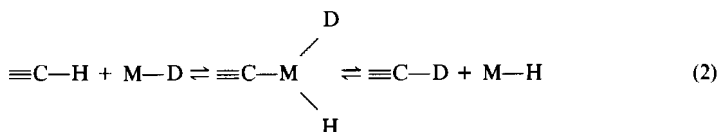
The reasons why bulky substituents on the phosphorus promote internal metalation are not entirely clear; it is not known if the important effects are thermodynamic or kinetic (10). In the case of thermodynamic effects, it is suggested that, for the phosphines with bulky substituents, internal metalation allows the phosphine to get closer to the metal and form a stronger metal-phosphorus bond. At the same time there is no appreciable loss of rotational entropy, since rotation is inhibited in the monodentate ligand, whereas for a nonsterically hindered phosphine, metalation would cause a considerable loss of rotational entropy, with no increase in the phosphorus-metal bond strength. If the effect is kinetic in origin, it is suggested that the free energy of activation is much more favorable for the compounds with bulky phosphine ligands than for those without such ligands, since the loss of entropy on forming the more constrained activated complex will be much less.

This work also shows that, in general, it is more difficult to form ring-closure products with palladium than with platinum. This finding probably can be explained by the greater difficulty in making palladium(II) complexes take part in oxidative addition to give the necessary palladium(IV) intermediate.

B. Hydrogen-Deuterium Exchange in Phosphine Ligands

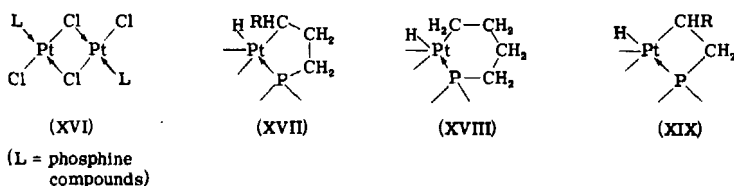
The catalyzed exchange of hydrogen in an organic molecule by deuterium from the solvent or from deuterium gas has been much used to study alkane activation by transition metal complexes; it is discussed

in detail in Section III. During such an exchange, activation and cleavage of the C—H bond by the metal to form a carbon–metal σ -bond must occur. The metal hydride formed will exchange the hydrogen for deuterium by, for example, dissociation of a proton and association of a deuterium from an acidic solvent, or the complex may be a polyhydride and deuterium will be already present on the metal, giving the following reaction:

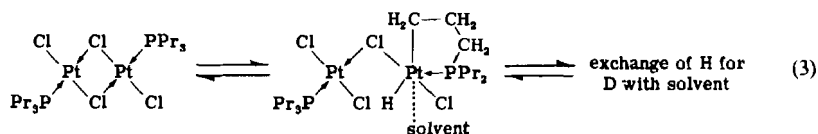


If the organic molecule is already a ligand on the transition metal, then, although the metal will be a catalyst for hydrogen–deuterium exchange, the number of exchangeable C—H bonds is clearly limited to those in the ligands. Such exchange reactions are well known for aromatic carbon–hydrogen bonds in arylphosphine ligands (76), and this work will not be reviewed here. There are few examples of alkyl groups in phosphines undergoing exchange. Moers and Langhout (68, 69) find that deuterium from deuterated ethanol solvent, or deuterium gas, enters the cyclohexyl groups of $\text{RuHCl}(\text{CO})(\text{P-cyclohexyl})_2$ or its osmium analog. Parshall (59) reports that deuterium enters the methyl groups of $\text{IrH}_5(\text{PMe}_3)_2$ when the complex is heated in benzene solution under an atmosphere of deuterium gas. If the activated complex for this exchange is monomeric, then it will contain a three-membered Ir—P—C ring; it is most probably polymeric or dimeric as was found for the only other suggested example of such a three-membered ring (see Section II, C).

Using the $\text{MeCO}_2\text{D}-\text{D}_2\text{O}$ system extensively studied for catalyzed hydrogen–deuterium exchange (see Section III), Masters and co-workers have obtained exchange in tertiary phosphine complexes of platinum(II) (57, 65). Dimeric complexes with a range of phosphine ligands (XVI; $\text{L} = \text{PEt}_3, \text{PPr}_3, \text{PBu}_3, \text{Pt-BuPr}_2, \text{Pt-Bu}_2\text{Pr}, \text{PPhEt}_2, \text{PPh}_2\text{Et}, \text{PPh}_2\text{Pr}, \text{PPhPr}_2, \text{and P-}t\text{-BuPh}_2$) have been studied. For the phosphines with n -alkyl groups [i.e., compounds XVI ($\text{L} = \text{PEt}_3, \text{PPr}_3, \text{PBu}_3$)], no exchange occurs in the ethyl group; the exchange is exclusively in the terminal methyl of the propyl group and predominantly at C-3 in the butyl group. After long reaction times, deuterium is also found at C-4 of the butyl group, but none is found at C-2 or C-1. This is clear evidence that the preferred activated complex has a five-membered ring (XVII), that the six-membered ring (XVIII) is formed but much less readily, and that, for these compounds, the four-membered ring (XIX) is not formed. The presence of phenyl groups in the phosphine has no effect; com-



pounds XVI with $L = \text{PPhEt}_2$ or PPh_2Et , like that with $L = \text{PEt}_3$, do not undergo exchange, and compounds XVI with $L = \text{PPr}_3$, PPhPr_2 , or PPh_2Pr all undergo H—D exchange exclusively at C-3 at approximately equal rates. The bulky tertiary butyl group in the ligand, however, has a marked accelerating effect, as it did in the compounds discussed in Section II,C. Compounds XVI with $L = \text{P}^t\text{-BuPr}_2$ and $\text{P}^t\text{-Bu}_2\text{Pr}$ undergo H—D exchange at the C-3 position of the propyl group, at a rate 2.5 and 27 times faster, respectively, than when $L = \text{PPr}_3$. Also when there are two *t*-butyl groups in the ligand, then exchange at C-2 of the propyl group and of the hydrogen atoms of the methyl groups also occurs, i.e., complexes with four-membered rings (XIX) are being formed under the influence of a pair of bulky *t*-butyl groups in the phosphine. This work also indicates that a dimeric complex is necessary for H—D exchange to occur since exchange does not occur in the monomeric complexes *cis*- and *trans*- $[\text{PtCl}_2(\text{PBU}_3)_2]$. The mechanism suggested for this reaction is



involving oxidative addition to the Pt(II) to form a Pt(IV) hydride; this can then exchange hydrogen for deuterium with the solvent leading to H—D exchange in the phosphine. Further discussion about this mechanism is deferred until Section III.

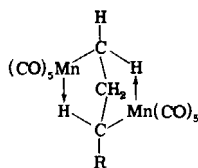
C. Compounds with Hydrogen in a Ligand Coordinated to a Transition Metal

Evidence of interactions with compounds having hydrogen in a ligand coordinated to a transition metal is very limited.

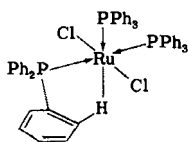
In order to explain the spectroscopic properties, particularly nuclear magnetic resonance, of the complexes $(\text{CO})_5\text{Mn}\cdot\text{CH}_2\cdot\text{CH}_2\cdot\text{CHR}\cdot\text{Mn}(\text{CO})_5$ ($R = \text{H}$ or Me), King (58) postulated an interaction between the hydrogen atoms of the alkyl chain and the manganese atoms. In the

structure proposed (XX; R = H or Me) the manganese must be the donor atom as it already has 18 valence electrons. Crystal structure determinations are required to provide unambiguous evidence of the existence of organic hydrogen in the coordination sphere of the metal. It is possible that this will happen in so-called "coordinatively unsaturated" complexes, that is, in compounds that do not have enough ligands to fill all the coordination sites around the metal. The crystal structure of such a ruthenium(II) complex, $\text{RuCl}_2(\text{PPh}_3)_3$, that has only five ligands was determined in 1965 by La Placa and Ibers (61). The ruthenium is in the center of an octahedron, one of the octahedral sites being filled by an ortho-hydrogen of one of the phenyl groups of one of the phosphine ligands (XXI). The Ru—H distance was estimated to be 2.59 Å, which is about the expected value for the sum of the van der Waals radii, and the authors observe that "there does not appear to be any basis for postulating any interaction between the ruthenium and the hydrogen." Similar structures have been reported for $\text{PdI}_2(\text{PMe}_2\text{Ph})_2$ (3), $\text{RuClH}(\text{PPh}_3)_3$ (91), and $\text{Rh}(\text{SiCl}_3)\text{ClH}(\text{PPh}_3)_2$ (70). In all these structures the metal-hydrogen distances are in the range 2.6–2.8 Å, and any interactions can only be extremely weak.

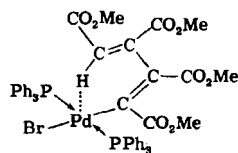
An interaction of an organic hydrogen and a metal was clearly indicated in the crystal structure of $\text{PdBr}(\text{PPh}_3)_2[(\text{CCO}_2\text{Me})_4\text{H}]$ (XXII) (79). Here the vinylic hydrogen is in the fifth coordination site of the palladium, and the Pd-H distance of 2.3 Å is much less than the sum of the van der Waals radii (3.1 Å).



(XX)



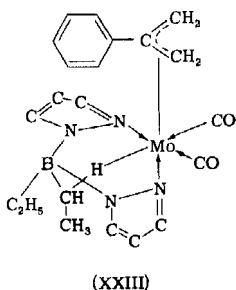
(XXI)



(XXII)

During a study of pyrazolylborato complexes of nickel (93) and molybdenum (94, 95), Trofimenko observed that one of the methylene hydrogen atoms of an ethyl group attached to the boron had an abnormal NMR chemical shift, and he suggested that this was because the hydrogen became more "hydridic" as a result of an interaction between the alkyl hydrogen and the transition metal. Recently, the crystal structures of two of the compounds studied by Trofimenko have been determined by Cotton and his co-workers (14, 16). In the compound, (diethyl-di-1-pyrazolylborato) (*trihapto*-2-phenylallyl)(dicarbonyl) molybdenum (XXIII), there is unequivocal evidence of an interaction

between the aliphatic C—H bond and the molybdenum (16). The best estimate of the Mo—H distance is 2.15 Å, a shorter distance even than that for the palladium complex (XXII), and the interaction can be regarded as a three-center 2-electron bond involving the C, H, and Mo atoms. It enables the molybdenum to achieve an 18-electron configuration. It has also been shown (14) that this C—H—Mo interaction is strong enough to compete with a possible extended interaction in a polyolefinic ligand. In compound XXIII the only means by which the molybdenum can achieve 18 valence electrons is by the C—H—Mo interaction. The crystal structure of the related compound, where the C₇H₇ ring replaces the phenylallyl group, shows a C—H—Mo interaction that is even stronger than in compound XXIII and the C₇H₇ ring is a 3-electron donor, i.e., this compound prefers the structure with a C—H—Mo bond and a η^3 -C₇H₇ ring to the structure without a C—H—Mo bond with a η^5 -C₇H₇ ring.

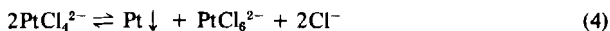


III

CATALYSIS OF HYDROGEN-DEUTERIUM EXCHANGE IN ALKANES AND RELATED COMPOUNDS

A. Exchange in the Benzene Ring Catalyzed by Platinum(II)

Much of the work on the catalytic activation of C—H bonds in alkanes follows from the important observation of Garnett and Hodges (21) that, in the presence of the PtCl_4^{2-} ion, aromatic compounds exchange hydrogen with deuterium in the $\text{D}_2\text{O}-\text{CH}_3\text{CO}_2\text{D}$ solvent. Temperatures in the range 80°–100°C are used and the solvent also contains a mineral acid to stabilize the platinum(II) from disproportionation:



The reaction of benzene has been much studied; the exchange rate was found to be proportional to both the concentration of benzene and the concentration of the PtCl_4^{2-} ion and inversely proportional to the concentration of chloride ion added to the reaction mixture (49). The dependence of the rate on the acidity of the medium was found to be more complicated: the rate increased and then decreased as the acetic acid concentration increased. The factors that were thought to be involved in producing this effect included the precipitation of platinum by Eq. (4) at low acidities, changes in solubility of the reactants, changes in the dielectric constant of the medium, and competition by the normal acid-catalyzed exchange. It was concluded that the metal-catalyzed exchange was not acid-catalyzed. It was also found that the reaction is not catalyzed by Pt(IV); if H_2PtCl_6 is used, there is an induction period while some of the H_2PtCl_6 is reduced to Pt(II) and some of the benzene is oxidized to chlorobenzene. This reaction is discussed further in Section IV, A, 1.

The relative merits of two possible reaction schemes have been discussed (20). The schemes considered involve either an associative π -complex (Fig. 1) or a dissociative π -complex (Fig. 2). These figures are drawn essentially as given by Garnett (20); they have been modified to include solvent molecules to fill and vacate coordination sites as required, and to make all the catalytic cycles in this review as comparable as possible.¹ It should be noted that these catalytic cycles for H—D exchange are symmetrical, the second half of the cycle being the reverse of the first half with deuterium instead of protium.

In both the associative and dissociative schemes, the first step of the catalytic cycle, at step 2 of Figs. 1 and 2, is the complexing of benzene, using its π -electrons, to platinum. The number of π -electrons involved in this bond is not known. If the complex is to have 18 or 16 electrons in its valency shell, and there is no reason to suppose that this reaction differs significantly in this respect from all other homogeneously catalyzed reactions (92), then the benzene is a 4- or more likely a 2-electron donor.

The mechanistic pathways then diverge. By the associative scheme, a solvated deuteron attacks the π -complexed benzene (Fig. 1, step 3). A proton is then lost (step 4), as is deuterated benzene (step 5) with regeneration of the catalyst. The intermediate produced at step 3 is similar to that of a conventional electrophilic attack at benzene, except

¹ In Figs. 1 to 4 and 7, solvolysis of one of the chloride ligands of the PtCl_4^{2-} ion is given as the first step in the reaction schemes. Complex $\text{PtCl}_3\text{-solvent}^-$ is then used as the catalyst. Evidence presented herein indicates that solvolyzed species are most probably the catalysts for the H—D exchange.

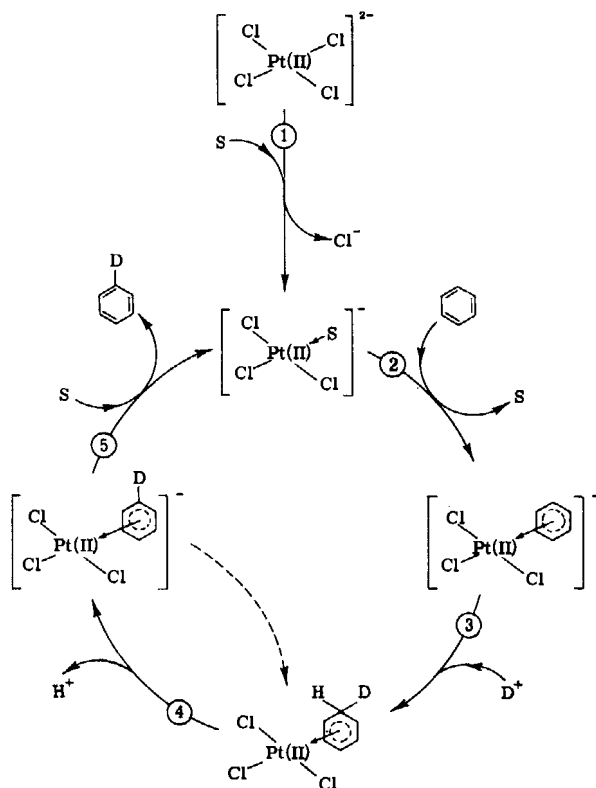


FIG. 1. Associative π -complex reaction scheme for H—D exchange in benzene. (S = acetic acid or water.) [Based on Garnett (20).]

that the benzene is complexed to platinum. The platinum is able to activate an unsaturated ligand to electrophilic attack by increasing the negative charge on the ligand by π -back donation (45).

If the mechanism is dissociative (Fig. 2), then oxidative addition occurs (step 3) to give a platinum(IV) hydride. This can then lose HCl (step 4) and gain DCl (step 5), to and from the solvent. The platinum(IV) deuteride can then revert to a π -complex with deuterium in the aromatic ring (step 6), and this deuterated benzene is lost (step 7) with regeneration of the catalyst.

Because substituted benzenes show a pronounced ortho-deactivating effect (50) and also because substituents such as nitro groups do not appreciably affect the exchange rate, Garnett favors the dissociative mechanism (Fig. 2).

The experimental results with benzene show one further important feature, namely, multiple exchange (*1*). Thus, several deuterium atoms enter the aromatic ring during a single residence on the catalyst. For benzene the multiple exchange factor (*M*) is ~ 4 . This can occur, for either scheme, by the complexes cycling round the dotted pathway (Figs. 1 and 2) before completing the main cycle. Also if *M* is >1 , the rate-limiting step must be the initial complexing reaction (Figs. 1 and 2,

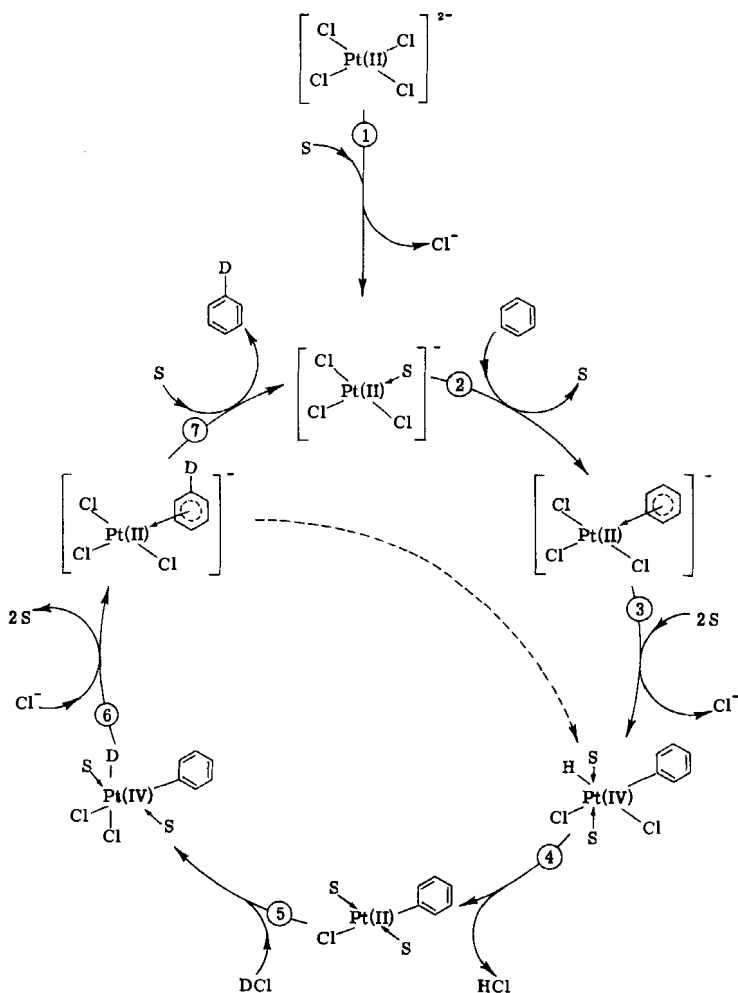


FIG. 2. Dissociative π -complex reaction scheme for H—D exchange in benzene. (S = acetic acid or water.) [Based on Garnett (20).]

step 2) or the complex formed at step 2 is a stable species and most of the benzene must be converted into it. As the concentration of platinum(II) was much less than the concentration of benzene, it was assumed that step 2 is rate-limiting.

Also, if $M > 1$, the reaction is not acid-catalyzed since the steps involving H^+ (or D^+) are all fast.

A recent study by Gold and his co-workers (5) on the catalysis by the tetrachloroplatinate(II) ion of the exchange of tritium between benzene and water throws some doubt on Garnett's conclusions. It was possible for this study to be carried out with water as the solvent at a temperature of $50^\circ C$, as the tritium tracer technique enables initial rates of very slow reactions to be measured. The main experimental findings of Garnett and Hodges are confirmed; the rate is proportional to $[C_6H_6]$, $[PtCl_4^{2-}]$, and $[Cl^-]^{-1}$. However, Gold also finds that the exchange rate is dependent on $[H^+]$. This is incompatible with multiple exchange, a feature that cannot unfortunately be investigated by Gold's tracer method. It must mean, therefore, that the exchange has different mechanisms in the two solvents, water and aqueous acetic acid, or, as Gold suspects, the observations of Garnett and Hodges do not necessarily lead to the mechanistic conclusion drawn by them. From the observed reaction orders, Gold finds that the stoichiometry of the activated complex at low acid concentrations is $\{C_6H_6, PtCl_3^-, H^+, \pm n\text{-solvent}\}$, and at high acid concentrations it is $\{C_6H_6, PtCl_3^-, \pm n\text{-solvent}\}$. This most probably means that at low acidities the rate-limiting step is a protonation, and at high acidities an earlier step in the reaction sequence becomes rate-limiting. Two reaction schemes compatible with these observations are suggested and are given in Figs. 3 and 4. The schemes are as given by Gold, with solvent molecules explicitly included to retain 16 or 18 electrons in the valency shell of the platinum. Predissociation of one of the chloride ions of the $PtCl_4^{2-}$ has been added, since, despite the comment to the contrary by Gold, the solvolyzed species have been found to be the catalysts for H—D exchange in alkanes (Section III,B,2).

In the catalytic cycle, the first step (Figs. 3 and 4, step 2) is the rapid formation of a benzene π -complex. In the first scheme (Fig. 3) this then rearranges (Step 3) into a second intermediate complex by a π - σ rearrangement of the aromatic ring, without transfer of the hydrogen onto the platinum. This step is the rate-limiting step at high acidities. The next step (step 4) is the protonation by D^+ , to give the complex illustrated (Fig. 3). This is the rate-limiting step at low acidities. The decomposition of this intermediate (steps 5, 6, and 7) are the reverse of steps 4, 3, and 2.

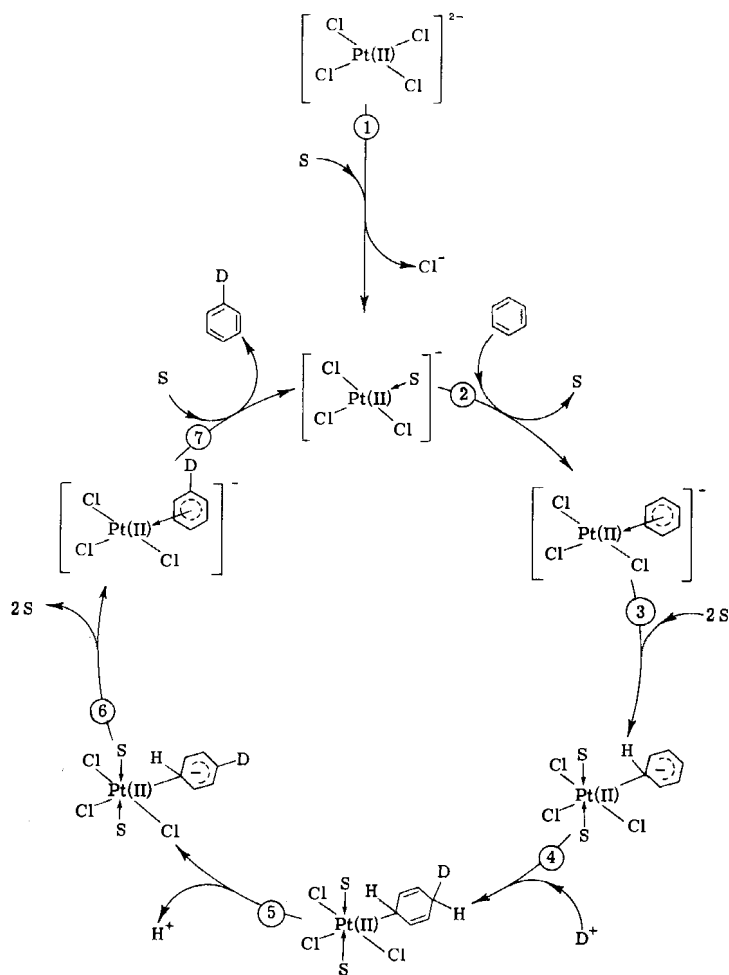


FIG. 3. Reaction scheme for H—D exchange in benzene. (S = water.) [Based on Gold (5).]

In the second mechanistic scheme (Fig. 4), after formation of the benzene π -complex, a π - σ rearrangement (step 3) occurs with transfer of the hydrogen to the platinum. The next step (step 4) is protonation of the platinum by D^+ to give a platinum phenyl dihydride.² This decomposes (steps 5, 6, and 7) by the reverse of steps 4, 3, and 2. For this

² It should be noted that this is formally a complex of Pt(VI); but the concept of oxidation state is not very appropriate here since oxidative addition of HCl is taking place.

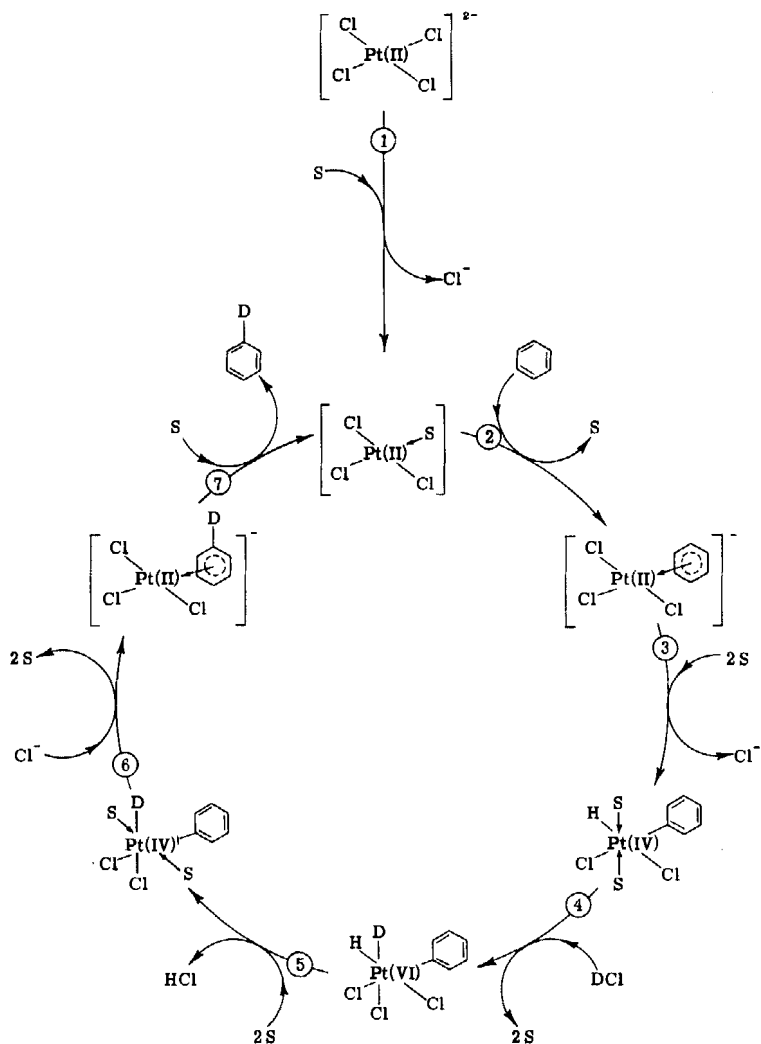


FIG. 4. Alternative reaction scheme for H—D exchange in benzene. (S = water.) [Based on Gold (5).]

mechanism also, step 4 would be rate-limiting at low acidities, and step 3 at high acidities. The dihydride formed by this mechanism is formally similar to that proposed by Falk and Halpern (19) for the H—D exchange in *trans*- $\text{PtHCl}(\text{PEt}_3)_2$.

Under certain conditions, the associative π -complex mechanism (Fig.

1), rejected by Garnett, also fits Gold's experimental results, although the rate-limiting step would then be the protonation (step 3) and not the formation of the π -complex (step 2). Of the schemes proposed by Gold, that involving the platinum hydrides (Fig. 4) is most compatible with other data (Section III). It is of interest to compare this scheme with that of Garnett (Fig. 2). Ignoring the dispute as to the rate-limiting step, they differ in only one respect: in the Garnett scheme, steps 4 and 5 involve removal of HCl followed by addition of DCl, and, in the Gold scheme, these two steps are reversed.³

It should also be noted that in these mechanistic schemes it has been assumed that the platinum catalyst is monomeric. Evidence presented later (Section III,B,2) indicates that dimeric species are important in catalyzing H—D exchange.

B. Exchange in Alkanes Catalyzed by Platinum(II)

The observations of Garnett and Hodges, that H—D exchange occurs in benzene and in the side-chains of alkylbenzenes (Section III,A), was reported at the Fourth International Congress on Catalysis in Moscow in 1968 (22). Soon after this, in 1969, Shilov and his colleagues (36) found that Garnett's catalyst system was active for H—D exchange in alkanes. Also in 1969, my colleague, Peter Wells, and I had obtained a research grant for studies in homogeneous catalysis including alkane activation. Ray Hodges applied to work with us; he seemed ideally suited for the work, and began investigating alkane activation that autumn (52). Since then work by Shilov and his co-workers, by us, and by others have considerably extended our knowledge of H—D exchange of alkanes and related compounds.

1. The Reaction Mixture

The reaction mixture is quite complex; there are five and sometimes six components. These are water, acetic acid, a mineral acid, the platinum(II) salt, the alkane (or other reactant), and sometimes an

³ The discrepancies between the results of Gold and those of Garnett (and others) are not resolvable on the evidence at present available. It is tempting to suggest that new features not present in the acid-solvent systems studied by all other workers become dominant in Gold's system, where the concentration of benzene is very low (the solvent is water) and comparable to the concentration of the catalyst. Certainly it is difficult to believe that the multiple-exchange parameters greater than 1 reported many times for exchange in benzene, and in many other compounds, can be attributed to experimental error, as Gold has suggested.

aromatic hydrocarbon. The water is the source of the deuterium, and, hence, deuterium oxide is used. Acetic acid is mixed with the water to produce a solvent for both the inorganic platinum salt and the organic reactant and to make the solvent acidic. An acidic solvent is required to suppress the disproportionation of the tetrachloroplatinate(II) ion according to Eq. (4) (32). This disproportionation gives platinum(IV) and platinum metal, both of which are unreactive as catalysts for the exchange reaction. The rate of H—D exchange in pentane is found to be a maximum with about 50 mole% acetic acid in water and to fall off at both lower and higher acid concentrations (53). This is the same as had been observed for the exchange in aromatic compounds (49, 51), and it occurs because hydrocarbons are only sparingly soluble in solvents with a high water content and the dielectric constant of the medium falls with increase in the acetic acid concentration.

In aqueous acetic acid, the disproportionation of the platinum still occurs quite rapidly, and it can be suppressed further by adding mineral acid. Hydrochloric acid is often used, but this has a disadvantage in that the exchange rate is inversely proportional to the chloride ion concentration. Perchloric acid has been found to be more satisfactory (53). The platinum(II) catalyst most used is sodium or potassium tetrachloroplatinate(II). An aromatic compound added to the reaction mixture also inhibits disproportionation of the platinum(II) complex—benzene, pyrene, and other aromatics have been used. A comparative study of the effect of various aromatics on the H—D exchange in alkanes has been carried out (53). Even under optimum conditions, the disproportionation [Eq. (4)] still takes place, and the catalytic platinum(II) is slowly removed from the reaction mixture. To get useful rates of exchange in alkanes, temperatures of 100° to 120°C have to be used, and the disproportionation rate increases with temperature.

In addition to exchange of the protium (called hydrogen in this review) in the alkane by deuterium from the solvent, hydrogen atoms in any added aromatic compound will also exchange. Hence to avoid dilution of the system by protium the aromatic used should be fully deuterated (e.g., C_6D_6). The hydroxyl hydrogen of acetic acid exchanges with the water, and CH_3CO_2D is used if the maximum amount of deuteration is an objective of the experiment. At 120°C, the concurrent platinum or acid-catalyzed exchange of the hydrogen atoms in the methyl group of the acetic acid cannot be ignored, and, for extensive deuteration of the alkane at the higher temperatures, perdeuterioacetic acid should be used. Oxygen gas also inhibits the disproportionation [Eq. (4)] (56, 96), and reaction tubes are sealed without evacuation prior to shaking in a thermostat tank. A typical reaction mixture might contain 0.02 *M*

PtCl_4^{2-} , 0.2 M DClO_4 , 0.3 M alkane, and 0.05 M pyrene in 50 mole% $\text{CH}_3\text{CO}_2\text{D}$ in D_2O .

2. The Platinum(II) Catalyst

It appears that platinum must be in the oxidation state of 2+ to be catalytically active. Platinum(IV) is inactive, and if a platinum(IV) salt is used (e.g., H_2PtCl_6), then an induction period is observed while platinum(II) is being produced, before any appreciable exchange occurs (96), just as was found for H—D exchange in aromatic hydrocarbons (49). Platinum metal is also totally inactive in this aqueous acetic acid solvent. The lack of reactivity of platinum(IV) and platinum(0) is readily apparent from the fact that exchange ceases when the disproportionation [Eq. (4)] takes place, i.e., when Pt(II) has been converted to Pt(IV) and Pt(0). Also two platinum(0) complexes [$\text{Pt}(\text{PPh}_3)_3$ and $\text{PtCO}(\text{HCl})_2$] have been examined as catalysts and found to be inactive (96). As the initial step in the exchange is a nucleophilic attack by the alkane on the metal, the platinum needs to be an electron acceptor and presumably platinum(0) is too weak an acceptor. Platinum(IV) complexes cannot be catalysts as Pt(IV) already has 18 electrons in its valency shell and cannot take part in an oxidative addition during the catalytic cycle (92).

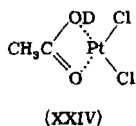
The activity of the platinum(II) catalyst is very dependent on the ligands surrounding it. When the bromoplatinate(II) ion is used, the exchange rate in ethane and other alkanes is reduced at least fivefold (55). Exchange rates using K_2PtI_4 as catalyst are even slower, and $\text{K}_2\text{Pt}(\text{CN})_4$ is inactive (96). Other "softer" (77, 78) ligands (e.g., PPh_3) on the platinum have been found to inhibit almost completely exchange in benzene (48). By contrast, catalysts of the form $\text{PtCl}_{x\text{solvent}}^{(x-2)-}$ ($x + y = 4$), i.e., where chloride has been replaced by solvent molecules, were more active than PtCl_4^{2-} (see in following) (54).

The experimental evidence indicates quite clearly that the "harder" the ligands the higher the activity. The hardness of bases (ligands) of interest increases in the order: $\text{CN}^- < \text{phosphines} < \text{I}^- < \text{Br}^- < \text{Cl}^- < \text{H}_2\text{O}$. This is the same as the order of the trans effect of these ligands (42, 43). The "hardness" and the trans effect are both measures of the same property, namely, the ability of the ligand to π -bond to the "soft" acid, platinum(II). As the ligand gets harder, its π -bonding capability decreases, and its ability to labilize ligands in the trans position of the square-planar platinum(II) complex also decreases.

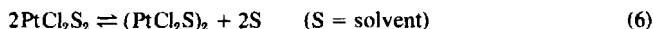
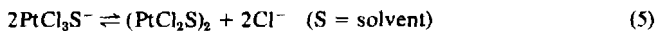
Clearly, ligands that least perturb the electron density elsewhere in the complex are the best here. There are several reasons why this should be so, although the relative importance (or even relevance!) of

them is not known. The bond formed between a catalyst molecule and a reactant molecule must be of just the right strength. It must not be too weak, or else no interaction will occur, nor must it be too strong, or the reactive intermediates will become stable compounds. The ligands affect this bond to the reactant molecule by helping to attain the electron density on the metal at the level required for catalysis. When an alkane reacts it must do so by losing a hydrogen to give an alkyl group σ -bonded to platinum. Soft bases attached to platinum stabilize platinum-carbon bonds (44), and it may be that only with hard bases is the platinum-carbon bond sufficiently reactive to give products. The ability of the metal to assist in breaking a C—H bond in an alkane to give an alkyl group is also related to the promotion energy of Pt(II) to Pt(IV) which must occur when forming the alkyl intermediate. Soft ligands may remove electron density from the metal and thus make the promotion energy too high (99).

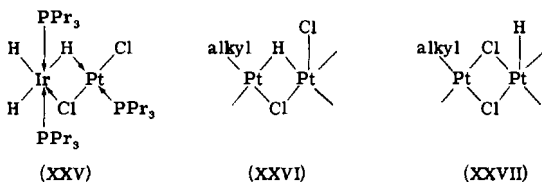
A further important factor may be that for the "soft" acid, platinum(II), the stability of the complexes decreases as the ligand base gets harder, i.e., stability decreases in the order: $I^- > Br^- > Cl^-$. For this reaction, solvolysis of one or more of the ligands of $PtCl_4^{2-}$ to give species such as $PtCl_3S^-$ and $PtCl_2S_2$ may be an essential step in forming a catalytic complex. This solvolysis does occur (53, 96), the reaction is inversely proportional to $[Cl^-]$, and a detailed mathematical analysis of the kinetic results (53) shows that the most important catalytic species is $PtCl_2$ solvent₂. Additional evidence comes from other experiments in which chloride ligands were replaced by solvent in the platinum complex, and these new complexes (of average composition $PtCl_{3.3}^{0.3-}$ and $PtCl_{2.3}^{0.3-}$) used as the catalyst were found to give exchange rates, respectively, 1 to 2.5 and 1.5 to 3.5 times those of $PtCl_4^{2-}$ (54). The acetic acid may additionally stabilize the catalyst by forming a weak chelate ring with the $PtCl_2$ (96):



A final reason for the need for 'hard' ligands is that it is these ligands that can form bridges to give dimeric complexes, and dimeric complexes may contribute to the catalytic activity in these reactions. The participation of dimeric species, formed for example, by

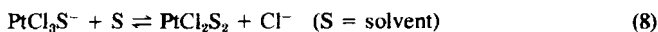
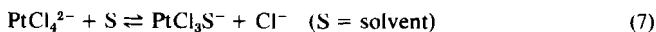


is indicated in the analysis of the kinetics by Hodges *et al.* (53), and it was suggested that such species may be responsible for multiple exchange (see Section III,B,3). The recent work of Masters and his co-workers (57, 60, 64, 65) (Sections II,B and III,C) indicates that dimeric complexes are of importance. It is significant that exchange occurs in the alkyl chain of soft phosphine ligands attached to platinum, but the complexes involved are dimers with bridges of hard chloride ligands. Masters and his colleagues (101) have recently studied hydride exchange between iridium and platinum and have obtained a mixed metal-hydrido complex (XXV) with a hydrido bridge. They suggest that facile hydride transfer could mean that complexes of the type XXVI and XXVII may be involved in H—D exchange, oxidative addition and exchange of hydrogen for deuterium of the solvent taking place at different platinum atoms.



3. The Mechanism of the Reaction

Hydrogen–deuterium exchange in alkanes shows the same dependence on the composition of solvent, and concentration of mineral acid, of platinum(II) and of chloride ions as does the exchange in aromatic hydrocarbons. The dependence of the exchange rate on solvent composition has been discussed in Section III,B,1. The rate is independent of mineral acid concentration, increases nonlinearly with increase in the concentration of platinum(II), and decreases nonlinearly with increase in the concentration of chloride ions (53). The nonlinear dependences are due to the solvolysis of the PtCl_4^{2-} ion:



(XXVIII)

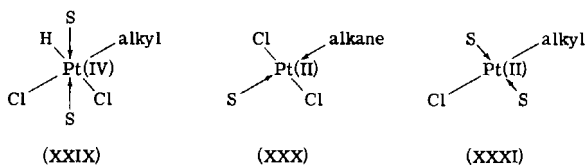
Analysis of the results indicates that the complex XXVIII is the major catalytically active species together with some dimer [Eqs. (5) and (6)]. Apparent orders of 0.62 with respect to K_2PtCl_4 and -0.56 with respect to Cl^- ions have been calculated (96).

All the evidence obtained so far indicates that, for this exchange,

aromatic compounds and alkanes behave in an identical manner, i.e., the mechanism of the exchange in alkanes parallels that in aromatic compounds. The favored scheme is the dissociative mechanism of Fig. 2, with benzene replaced by alkane. Whether or not Gold's criticisms of this mechanism as applied to benzene (Section III,A) applies to alkanes is not known, as Gold has not carried out any studies of hydrogen-tritium exchange in alkanes (33).

If the mechanism is as shown in Fig. 2, activation of the alkane occurs by oxidative addition to give the platinum(IV) alkyl hydride (XXIX). Gol'dshleger *et al.* (35) have obtained evidence that platinum alkyls are involved, by studying the alkyl exchange between K_2PtCl_4 and alkylmercury(II) bromide under conditions where hydrogen-deuterium exchange is also possible. The deuterium content and distribution in the alkanes produced are similar to those found when alkane is the reactant. As alkyl exchange between mercury and platinum is known to occur, the interpretation of these results is that the exchange must go through the same alkyl intermediate.

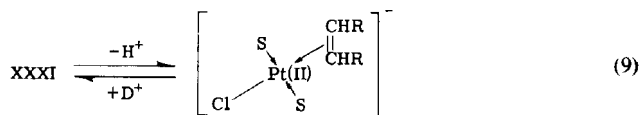
Less is known about the interactions that occur between an alkane and platinum(II) prior to the formation of the alkyl intermediate. In Section III,B,4, a correlation between exchange rate and ionization potentials of the alkanes is discussed. Ionization potential is a "1-electron property," i.e., it is a measure of the energy of the highest occupied molecular orbital in the molecule (17). Therefore we must not think of alkanes, as is most commonly done, in terms of a localized bond model wherein pairs of electrons are localized between pairs of atoms, but rather in terms of the proper description using the true molecular orbitals. This is the fully delocalized molecular orbital model, wherein all the electrons are in extended molecular orbitals that belong to the whole molecule. The preliminary interaction is considered to be nucleophilic attack by the alkane at the platinum, the electrons involved being those in the highest occupied molecular orbital of the alkane. If the platinum compound is originally considered to be $PtCl_2solvent_2$ the intermediate (XXX), with platinum having 16 electrons in its valency shell, is thus formed. Subsequent steps in the reaction involve oxidative addition of the alkane to the platinum (step 3 of Fig. 2, with alkane replacing benzene) to give complex XXIX, followed by loss of HCl (step 4 of Fig. 2, with alkyl replacing phenyl) to give intermediate XXXI. This then gains DCl from the solvent (step 5 of Fig. 2, with alkyl replacing phenyl). Steps 6 and 7 complete the catalytic cycle. If the Gold mechanism (Fig. 4) applies, the gain of DCl (step 4 of Fig. 4, with alkyl replacing phenyl) and loss of HCl (step 5 of Fig. 4, with alkyl replacing phenyl) occur in reverse order.



Garnett's associative mechanism (Fig. 1) and Gold's mechanism that involves direct exchange in the aromatic ring (Fig. 3), both of which for benzene involve plausible intermediates, become much more difficult to formulate and, consequently, much less attractive when benzene is replaced by an alkane.

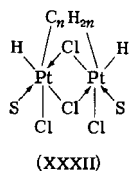
The multiple-exchange parameter for alkanes is greater than 1 [usually in the range 1.3 to 2.0 (53, 96)], and this is explicable if the rate of formation of the intermediate (XXX) is rate-limiting. Several steps in the exchange cycle (Fig. 2 *via* dotted pathway) can then take place before the alkane leaves the complex, as was suggested for aromatic compounds (Section III, A).

It has also been proposed (96) that multiple exchange occurs via formation of platinum-alkene complexes from the alkyl intermediate (XXXI):

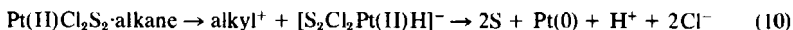


Even multiple exchange in methane could be explained this way. For methane, a carbene complex would be postulated, and such complexes are now known (87). One objection to the involvement of platinum-alkene complexes is that they are very stable and once formed might not be expected to react further, as was found when exchange in chloropropane was attempted (Section III, C) (55). Also the compound formed is a platinum(0) complex. A mathematical analysis of multiple exchange similar to that developed by Anderson and Kemball (1) has been carried out (82).

An attractive suggestion for the mechanism for multiple exchange, in the light of current knowledge, is the involvement of dimeric platinum complexes (53), the hydrocarbon interacting with both platinum atoms:



One final feature of the system is worthy of comment. Whatever the mechanistic pathway might be by which hydrogen–deuterium exchange takes place, it is remarkably selective. No hint of any side reactions leading to functionally substituted alkanes has been observed. This is a disappointing situation, as activation of alkanes to give functional derivatives is a much more useful reaction than hydrogen–deuterium exchange! It is hoped that, if alkyl intermediates are involved, some reaction might occur with the solvent to give alkyl acetates or that hydride transfer might occur,



particularly where R^+ is a stable carbenium ion (62). Even when the compounds adamantane (XXXIII), norbornane (XXXIV), protoadamantane (XXXV), triphenylmethane, and triptycene (XXXVI), all of which are known to give stable carbenium ions, are used, only the deuterated products are produced.



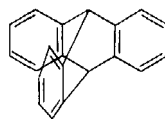
(XXXIII)



(XXXIV)



(XXXV)



(XXXVI)

If, as appears to be the case, alkyl intermediates are involved, it is surprising that they cannot be made to undergo some other reaction since such complexes are postulated as taking part in many other catalytic reactions. This inability to steer the reaction path away from hydrogen–deuterium exchange does leave one wondering if there is not some feature of the mechanism of the exchange that we have not yet recognized and which may invalidate part (hopefully not all!) of what has been written in this section.

4. The Relative Reactivity of Alkanes

The exchange of a considerable number of linear, branched-chain, and cyclic alkanes have been studied (53). The exchange rate increases with increase in the carbon chain length for *n*-alkanes (methane to hexane). It is found that there is a linear correlation between the logarithm of the exchange rate and the ionization potential of the alkane (Fig. 5; *n*-alkanes are plotted as circles). This correlation extends to aromatic compounds (Fig. 5; aromatic compounds are plotted as squares) and is evidence that alkanes and aromatic compounds react by a common mechanism. Indeed, the least reactive aromatic, benzene, is only about

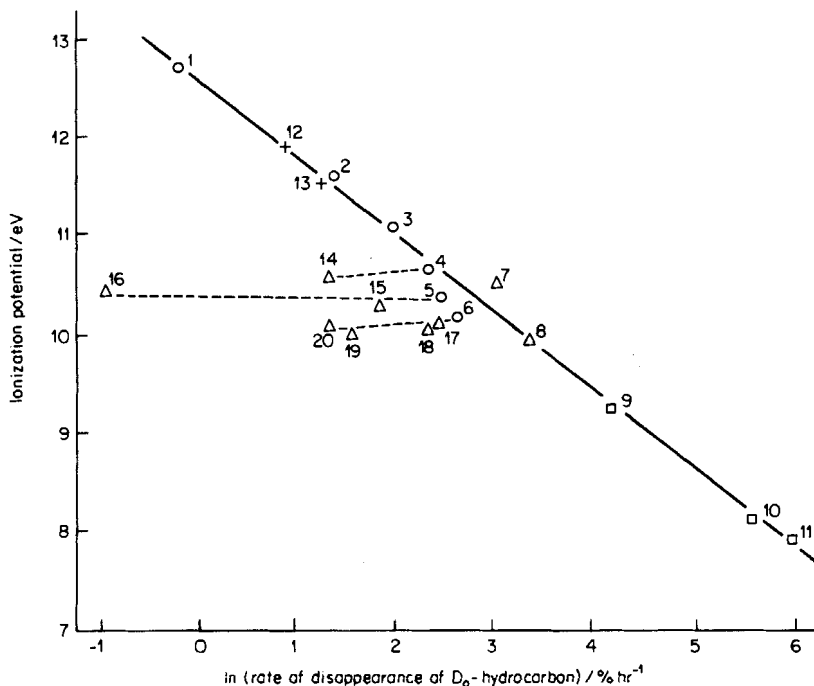


FIG. 5. Rate of H—D exchange versus ionization potential of alkanes and aromatic compounds: 1 = methane; 2 = ethane; 3 = propane; 4 = *n*-butane; 5 = *n*-pentane; 6 = *n*-hexane; 7 = cyclopentane; 8 = cyclohexane; 9 = benzene; 10 = naphthalene; 11 = phenanthrene; 12 = 2,2-dimethylbutane (see text); 13 = 1,1-dimethylpropylbenzene (see text); 14 = 2-methylpropane; 15 = 2-methylbutane; 16 = 2,2-dimethylpropane; 17 = 2-methylpentane; 18 = 3-methylpentane; 19 = 2,3-dimethylbutane; 20 = 2,2-dimethylbutane.

twice as reactive as the most reactive alkane, cyclohexane. The ionization potential correlation must be used with care. The potential needed is that for an electron in an orbital that is much involved in the carbon-hydrogen bond that breaks and becomes carbon-deuterium. If this is done (55), then the exchange rates of the hydrogen atoms in the methyl groups of 2,2-dimethylbutane and 1,1-dimethylpropylbenzene (Fig. 5, plotted as crosses) fit on the linear alkane correlation line. Also steric effects are important in this reaction and these can upset a correlation with ionization energies.

The importance of steric effects is evident when branched-chain alkanes are studied; rates of exchange decrease with increase in branching (e.g., pentane, 2-methylbutane, and 2,2-dimethylpropane (Fig. 5, points 5, 15, and 16). The reactivity at different kinds of carbon atoms in

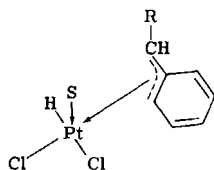
alkanes decreases in the order primary > secondary > tertiary. Both methyl and methylene groups adjacent to a quaternary carbon atom have very low reactivity (e.g., in 2,2-dimethylbutane). Even though they contain only methylene groups, the most reactive alkanes were cyclopentane and cyclohexane; it is not clear why this was so (53, 54).

Recently, the studies on cyclic alkanes have been extended and have shown that for cyclobutane the C—C σ -bond interacts with the platinum(II) (46). This is not too surprising since it had been shown earlier that, when cyclopropane interacts with platinum(II), a stable complex containing a four-membered Pt—C—C—C ring is formed (66). Cyclobutane has a much larger multiple-exchange factor ($M = 3.6$) than the other cycloalkanes (up to cyclooctane studied, $M = 1.4$ – 1.6), indicating a much stronger interaction between the cyclobutane and the catalyst than for the other cycloalkanes. This is also clearly so when *cis,anti,cis*-tetraphenylcyclobutane is used as the reactant; C—C bond cleavage occurs to give *trans*-stilbene as a product. Exchange studies on cycloheptane and cyclooctane show that, for the cyclic alkanes, the rates do not correlate with ionization potentials; steric factors are more important.

C. Exchange in Alkyl Groups Catalyzed by Platinum(II)

Hodges and Garnett observed that exchange in alkylbenzene involved not only the ring hydrogen atoms but also those of the alkyl chains (50). Exchange occurred at all the carbon atoms of the alkyl chain; for ethylbenzene the percentage of deuterium on the α - and β -carbon atoms was about the same, and for *n*-propylbenzene the percentage of deuterium in the alkyl chain was highest in the terminal methyl group. Subsequent studies (21, 26, 53) on a whole range of alkylbenzenes has confirmed these initial observations: exchange occurs most extensively with the ring hydrogen atoms, and of the hydrogens of the *n*-alkyl chain those α to the ring and in the terminal methyl group exchange more extensively than those on the carbon atoms in the middle of the chain.

Detailed studies on the products of exchange in toluene and polymethylbenzenes (25), together with the extensive exchange at the α -carbon in other alkyl chains indicates that exchange is being facilitated by the proximity of the aromatic ring. This finding is explained if the π -complex initially formed undergoes oxidative addition (Fig. 2, step 3) to give a π -benzylic intermediate,



(XXXVII)

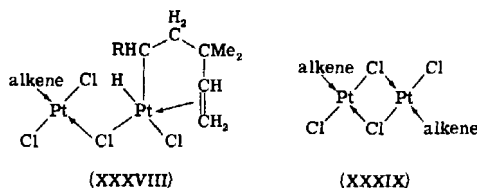
by loss of the α -hydrogen of the alkyl chain. Exchange at the β - and subsequent carbon atoms of the alkyl chain occurs by a process independent of the exchange in the ring; i.e., the catalyst causes exchange in the alkyl chain just as it does for an alkane. If this is so, then the most extensive exchange is to be expected, as is found, in the terminal methyl groups, since exchange on the primary carbon atoms was found to be most extensive for alkanes.

Although the exchange processes in the ring and in the alkyl chain are independent, it is possible that the alkylbenzene remains π -bonded by the ring to the platinum while exchange in the side chain is taking place (26). Although this may be so, it should be noted that, as just discussed, exchange is more extensive in the terminal methyl group than on the methylene groups of the alkyl chain for all the alkylbenzenes from propylbenzene to nonylbenzene. This contrasts with the work discussed in the following and elsewhere in this review where the favored products are those formed from five-membered ring intermediates. A suggestion that the mechanism of exchange could involve reversible dealkylation has since been shown to be incorrect by carbon-14 studies (23, 25).

Exchange in a number of halogeno-substituted alkanes have been correlated with the ionization energies of the molecules (55). When the first ionization potential is associated with a molecular orbital centered on carbon-hydrogen bonds, then hydrogen-deuterium exchange occurs, but when this potential is associated with electrons of the halogen atom, then displacement of the halogen occurs. 1-Fluoropentane, 1-fluorohexane, and 1-fluorooctane all undergo hydrogen-deuterium exchange at rates somewhat slower than the alkanes. 1-Chloropropane lost HCl and the propene formed reacted with the platinum(II) catalyst to produce a solution of a yellow complex, and exchange was completely inhibited. 1-Chlorobutane and higher chloroalkanes exchanged hydrogen for deuterium at comparable rates to the fluoroalkanes. For the chloroalkanes, chlorine-36 studies show that chloride exchange with the chloride ions on the platinum(II) and in solution is taking place concurrently with the H—D exchange. No linear monobromoalkane nor monoiodoalkane undergoes hydrogen-deuterium exchange. Platinum bromide and platinum iodide complexes are formed and these are of low catalytic activity.

Exchange rates in a number of halogeno-substituted methanes and ethanes have been correlated with Taft's σ^* parameters (80).

Alkenes of the type $\text{RC}(\text{CH}_3)_2\text{CH}=\text{CH}_2$ ($\text{R} = \text{Et, Pr, or Bu}$) undergo hydrogen-deuterium exchange in the side chain (60, 64). Alkenes with geminal methyl groups were chosen, so that platinum-allyl type complexes could not form and isomerization of the alkene could not occur. By using the type of mathematical analysis developed earlier (53) on the kinetic results, the authors concluded that the catalyst is the dimeric species formed by Eqs. (5) and (6). The exchange in the alkyl part of the molecule is almost all at C-5, indicating that intermediates containing a five-membered ring with the alkene π -bonded to the platinum (XXXVIII) are involved. The preference for five-membered ring systems is emphasized elsewhere in this review. Furthermore, complexes XXXIX could be isolated, they are very similar to the phosphine complexes in which $\text{H}-\text{D}$ exchange also occurs (57, 65), as discussed in Section II,B.



D. Exchange Catalyzed by Other Transition Metal Complexes

In their first note (36), Shilov and his co-workers reported that a little $\text{H}-\text{D}$ exchange occurred in methane using $\text{CoH}_3(\text{PPh}_3)_3$ as the catalyst. They pointed out that the small amount of CH_3D produced may have been formed during the decomposition of the complex, and further studies are needed to confirm that this complex is a catalyst.

Iridium and rhodium chloro complexes have been found to catalyze $\text{H}-\text{D}$ exchange in alkanes (6, 28). Detailed results have not been published. Alkylaromatic compounds react with a solution of Na_3IrCl_6 in aqueous acetic acid and exchange hydrogens of the ring and side chain (27). The deuterium distribution is similar to that found using the platinum(II) catalyst. The exchange on iridium(III) is substantially slower than on platinum(II), but the solutions have a better thermal stability and higher temperatures (130°C) can be used. By using still higher temperatures ($150^\circ\text{--}170^\circ\text{C}$), extensive exchange (up to 70%) of hydrogen in the linear alkanes, methane to heptane, cyclopentane, and cyclohexane has been observed. The optimum reaction conditions are

somewhat different from those for the platinum(II) catalyst; for iridium(III) catalysis the acetic acid concentration in the solvent is lower and added mineral acid is not needed.

The only alkane used in the study using rhodium trichloride as a catalyst (6) is cyclohexane. This system is intermediate in stability between that of Ir(III) and Pt(II), and the exchange rate is slower. The distribution of deuterium in the side chain of alkyl aromatics is as found on the other catalysts, and the rate of cyclohexane exchange is very much slower than that of benzene.

Exchange in the alkyl side chain of the phosphine $(C_6H_5)_2P(CH_2)_nCH_3$ has been reported to occur when a solution of the phosphine is treated with deuterium gas in the presence of the ruthenium(II) complex, $RuHCl(PPh_3)_3$ (76).

From the few results published, it would appear that the mechanistic pathway for hydrogen–deuterium exchange catalyzed by rhodium(III), iridium(III), and ruthenium(II) is the same as for platinum(II).

IV

OXIDATIONS OF ALKANES AND RELATED COMPOUNDS INVOLVING TRANSITION METAL COMPOUNDS

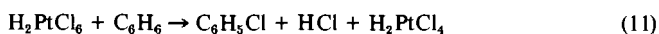
As discussed in Section III,B,3, no other chemical products are formed during the catalytic hydrogen–deuterium exchange. This exchange cannot take place without activating and breaking C—H bonds in the alkane; but to capitalize on this activation we need to be able to make products other than the deuteriated isomer of the alkane. The progress in this direction using soft precious metal complexes as catalysts has been disappointing. More useful chemical products are obtained using hard transition metal compounds. These two areas are the subject of this section.

A. Oxidation (Chlorination) of Benzene and Alkanes Using Platinum(IV)

1. Chlorination of Benzene

Hodges and Garnett (49) in the first full paper on hydrogen–deuterium exchange in benzene reported that if the platinum salt used is of platinum(IV) (i.e., H_2PtCl_6), instead of platinum(II), then the initial

reaction is the reduction $\text{Pt(IV)} \rightarrow \text{Pt(II)}$ with some of the benzene being oxidized to chlorobenzene:



Recent studies have shown that the reaction, as described by Eq. (11), also requires Pt(II) as a necessary catalyst (29, 84). A range of substituted benzenes has been examined, and by studying concurrent hydrogen–deuterium exchange, it was concluded that the two reactions had common intermediates (29). In this work aqueous acetic acid was used as the solvent, and reactions were followed by measuring the concentration of the chlorobenzene product. Of the several possible mechanisms for the oxidation that have been given (29), only one will be considered here; this is the one that has received substantial support from the most recent work (84). In this study, the loss of reactant benzene, the formation of product chlorobenzene, and the formation of platinum(II) were monitored as the reaction proceeded. Also aqueous trifluoroacetic acid was used as the solvent, as it is known that acetic acid is oxidized to chloroacetic acid by platinum(IV) (18).

The only oxidation product of any significance was chlorobenzene ($<1\%$ of the benzene gave biphenyl), and during the course of a reaction not all the benzene lost could be accounted for as chlorobenzene formed. Reduction of the reaction mixture with hydrazine hydrate gave

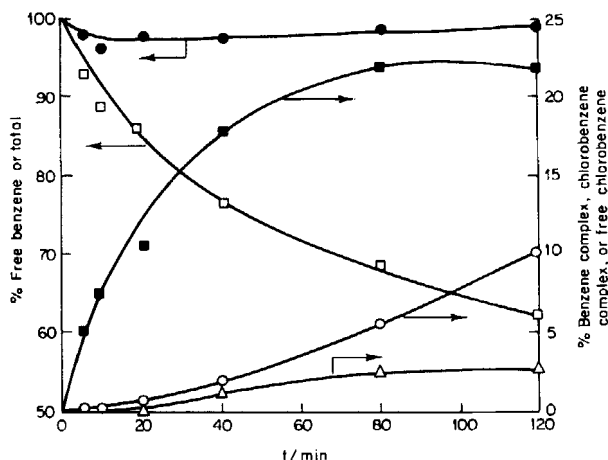
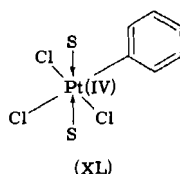


FIG. 6. Molar percentages of aromatic compounds in a typical reaction mixture at 120°C with reactants H_2PtCl_6 and benzene in water–trifluoroacetic acid solution: (\square) benzene; (\blacksquare) benzene complex; (\triangle) chlorobenzene complex; (\circ) chlorobenzene; (\bullet) total. [Reproduced from Sanders *et al.* (84).]

more benzene and chlorobenzene; this had been complexed as platinum–benzene and platinum–chlorobenzene. The concentrations of these complexes and of benzene and chlorobenzene during a reaction varied as shown in Fig. 6. Measurement of the concentration of platinum(II) formed during the course of reaction indicates that the complex with benzene is of platinum(IV). The reaction scheme for this oxidation is given in Fig. 7.⁴ Comparison of the reaction scheme for H—D exchange in benzene (Fig. 2) with Fig. 7 shows how much the two have in common. The two schemes are identical until step 5 when, in this oxidation (chlorination), chloride exchange between PtCl_6^{2-} and the platinum(II)–phenyl complex takes place, presumably via a bridged intermediate, and this is followed by ligand chlorination at step 6. Dichlorobenzene, which is detected at long reaction times, is formed by following the dotted reaction path in Fig. 7, and moving round the oxidation cycle twice before the product leaves the catalyst. The evidence indicates that the complex,



formed by reaction 5, is the major platinum–benzene complex in the system.

2. Chlorination of Alkanes

Alkanes appear to react with platinum(IV) in an identical manner to benzene (34, 84); chloromethane and chloroethane can be detected as the reaction products from methane and ethane, respectively. When propane, butane, or hexane is the reactant, the terminal chloro isomers predominate over the internal isomers. This was interpreted to mean that primary C—H bonds are the most reactive (34), but a more detailed study has shown that this conclusion does not necessarily follow from the experimental results (84). When cyclohexane is the reactant, dehydrogenation (or chlorination and then dehydrohalogenation) occurs to give benzene as one of the reaction products (29, 34, 84).

A noticeable feature of alkane chlorination is the very low yield of chloro products. Using hexane as the alkane, it has been shown (84) that

⁴ This, like other reaction schemes in this review, is not identical with that given elsewhere (29, 84). It differs in that chloride ions and solvent molecules are added and removed to make the intermediates in all reaction schemes as comparable as possible.

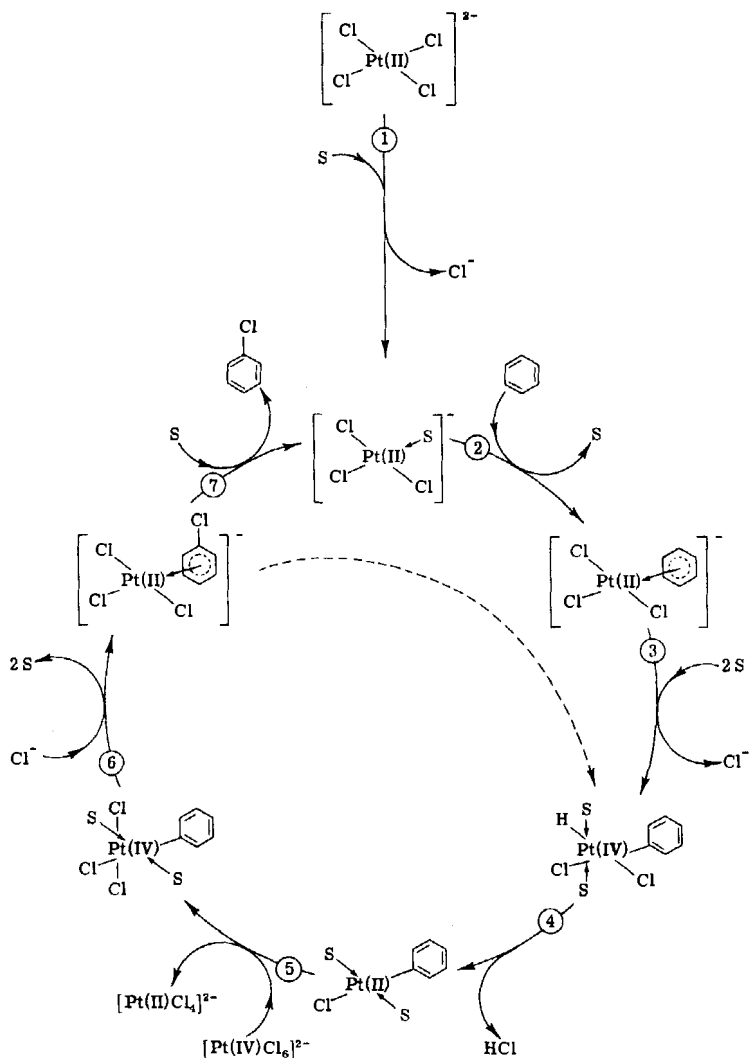


FIG. 7. Reaction scheme for the chlorination of benzene by the PtCl_6^{2-} ion. [Based on Garnett (29) and Sanders (84).]

the kinetics of reaction of alkanes exactly parallel the reaction of benzene in the early stages of reaction; the dependence on Pt(IV), Pt(II), and Cl^- concentrations being identical, and, hence, the oxidation of alkanes to chloroalkanes is by the reaction scheme of Fig. 7 with alkane replacing benzene. However, the yield of chlorohexanes is much lower than expected; for example, when 10% of the hexane had

disappeared the amount of 1-chlorohexane was only 0.7%, and the reaction mixture contained less than 0.1% of other compounds, namely, isomers of chlorohexane, isomers of dichlorohexane, hexanols, hexanones, hexyltrifluoroacetates, hexanoic acids, dodecane, or isomerization or dehydrogenation products of hexane. About 1% of what was thought to be a platinum-hexene complex was found, but about 90% of the hexane consumed had completely disappeared! A clue to where it had gone was obtained by measuring the amount of platinum(II) formed in the reaction. Every conversion of Pt(IV) to Pt(II) causes a 2-electron oxidation of hexane or one of its reaction products, and, hence, a measure of the amount of Pt(II) formed shows the amount of oxidation that has occurred. For every molecule of hexane consumed, 5–6 atoms of Pt(II) are formed; i.e., on average each hexane molecule that reacts undergoes five to six 2-electron oxidations. Studies with other alkanes showed the same feature; the chloroalkanes produced were themselves oxidized. The longer the alkyl chain, the more extensive this oxidation, e.g., for decane, each molecule consumed underwent, on average, seven 2-electron oxidations. If a branched-chain alkane was used, so that the scope for multiple oxidation was reduced, the ratio of platinum(II) formed to alkane lost was much reduced, e.g., for 2,2-dimethylbutane the ratio was 3:1, and 2,2-dimethylpropane was not oxidized by Pt(IV).

The much higher yields of 1-chloropropane than 2-chloropropane reported by Gol'dshleger *et al.* (34) do not arise necessarily from preferred attack at the terminal carbon of the alkane, as the internal isomers are themselves oxidized faster than the terminal isomer. If 1-chlorohexane or a mixture of 2- and 3-chlorohexanes was used as the reactant, then, when the 2- and 3-isomers had been consumed, 75% of the 1-isomer still remained (84). The ultimate oxidation product, carbon dioxide, was not formed, and it is thought that the major product from alkane oxidation are polychlorinated carboxylic acids formed by chlorination and reaction with the solvent. These acids are difficult to find in the reaction mixture and despite strenuous efforts have not been identified.

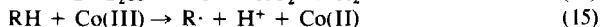
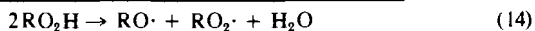
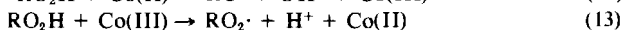
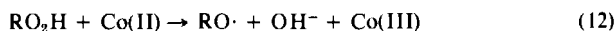
To obtain reasonable amounts of monochloroalkane, some means of preventing further reaction must be devised. The problem of stopping an oxidation at an intermediate product is very common; products of hydrocarbon oxidation are invariably more readily oxidized than the hydrocarbon itself.

Alkane chlorination is a stoichiometric reaction [such as Eq. (11)], and a Pt(IV) atom is lost each time a chloroalkane molecule is produced. Efforts to make it catalytic, by converting the Pt(II) formed back to Pt(IV), have so far been totally unsuccessful (86): added $K_3Fe(CN)_6$, $RuCl_3$, and $Fe(OH)(OAc)_2$ are without effect. Certainly a very subtle

reoxidation will be needed as the reaction product, Pt(II), is also the catalyst for the chlorination by Pt(IV). Therefore, if a too efficient reoxidation is found, it leaves no Pt(II) in the system and the reaction stops.

B. Oxidation of Alkanes Catalyzed by Cobalt(III)

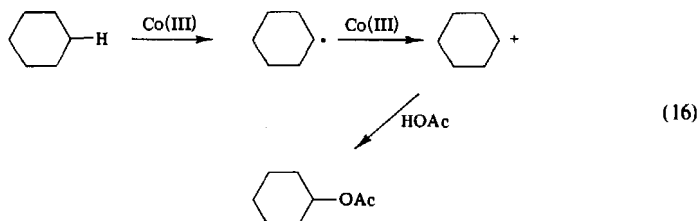
It is clear from a recent review of the mechanisms of metal-catalyzed oxidations of hydrocarbons (89) that by far the most extensive studies have been on the oxidation of alkenes and aromatic compounds; relatively little work on alkane oxidation is to be found. The studies on these reactions show that, if the reactivity is enhanced by a hard metal, it is often because the metal becomes involved in the free-radical reactions and generates further free radicals by the chain decomposition of hydroperoxides (39):



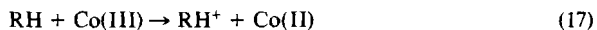
The possibility of a direct interaction [Eq. (15)], giving homolytic cleavage of the C—H bond to generate directly a free radical, has been suggested initially for aromatic compounds (2, 47), and it is reactions of this type that are of interest here.

Alkane Oxidations

Cooper and Waters (13) first reported the oxidation of cyclohexane by cobalt(III) perchlorate in aqueous acetonitrile to give a mixture of cyclohexanol, cyclohexanone, and adipic acid. A more detailed study of this oxidation (74), using cobalt(III) acetate in acetic acid at 80°C, both with and without oxygen, gives products, such as cyclohexylacetate, that can only be explained if there is a direct interaction of cobalt(III) with the C—H σ -electrons of the cyclohexane, as follows:



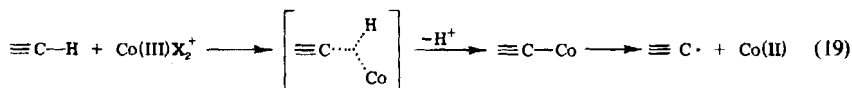
Additional evidence was obtained when the oxidation was carried out in the presence of copper(II) acetate, a common radical terminator. The oxidation proceeded unhindered and is not, therefore, dependent on hydrogen abstraction by free radicals. It can be represented by Eq. (15) or better by



n-Butane oxidation using cobalt(III) and oxygen has also been studied (73) at 100°C, which is below the temperature at which the catalyzed free-radical reaction occurs. The major products are acetic acid and other low carbon number carboxylic acids. *n*-Pentane gives similar products, but isobutane is of low reactivity, presumably because of steric interactions with the cobalt(III)-acetate complex. Much larger concentrations of cobalt(III) are used than in the higher-temperature reaction in which the cobalt decomposes hydroperoxides into radicals. For the high-temperature oxidation of butane, manganese catalysts are more efficient than those of cobalt, but the reverse is true for this low-temperature oxidation. The important factor appears to be the lower oxidation potential of the Mn(III)-Mn(II) couple (1.51 V) compared with that for Co(III)-Co(II) (1.82 V), implying that Mn(III) ions are not sufficiently strong an oxidant to abstract electrons from C-H σ -bonds. For alkanes and alkylbenzenes, tertiary hydrogen atoms are of low reactivity, and for the *n*-alkanes, butane is more reactive than pentane, and undecane is unreactive; this is a pattern of behavior inconsistent with a normal free-radical pathway for which increasing reactivity with increasing number of methylene groups is to be expected.

An interesting modification of the cobalt(III) acetate system is the discovery by Hanotier and his co-workers (41) that added strong acids much enhance the reactivity. With added sulfuric, trichloroacetic, methylsulfonic, or many other acids, alkanes could be oxidized by cobalt(III) acetate, both with or without oxygen, at 25°C. The reaction products in the absence of oxygen are acetic esters of alcohols, and in the presence of oxygen they are ketones. In both cases the products are a mixture of isomers, but there is a predominance of the isomer resulting from attack on the second carbon atom in the alkane chain, although this selectivity is lost with increase in temperature, the product distribution becoming almost statistical at 100°C. The conclusion from the position of substitution in the *n*-alkanes and branched alkanes is that the interaction between hydrocarbons and cobalt(III) depends greatly on steric factors. The reaction can be described by Eq. (15) or by Eqs. (17) and (18). The actual mode of interaction between cobalt(III) and the alkane has not been determined. It may be that an intermediate cobalt(III) alkyl is

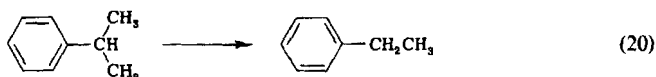
involved; the reaction is most probably like the large class of electrophilic substitutions by hard acids discovered by Olah (72) and his co-workers. It involves attack at the C—H σ -bond via a three-center transition state, leading to the cobalt(III)-alkyl complex that decomposes to a free radical and cobalt(II):



V

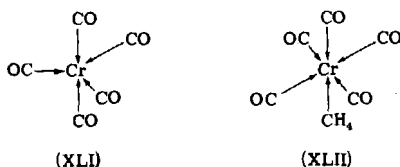
MISCELLANEOUS STUDIES INVOLVING ALKANE ACTIVATION

During a study of the reactions of aromatic hydrocarbons with the hydrides formed by reducing cobalt(III) acetylacetonate with triisobutylaluminum, Tyrlik and Michalski (98) observed that some of the cumene solvent is converted to ethylbenzene, e.g.,



It is suggested that this occurs by interaction of the isopropyl side chain with the cobalt complexes in solution, leading to C—C bond cleavage and subsequent hydrogenation (97).

Evidence of an interaction between a transition metal and methane has come from a rather unusual source (37). When Cr(CO)_6 is photolyzed in a solid methane glass at 20 K, the expected Cr(CO)_5 is not, as had been thought, of D_{3h} symmetry (XLI), but instead is $\text{Cr(CO)}_5\cdot$ methane in which the Cr(CO)_5 is of C_{4v} symmetry (XLII):



A solution of palladium(II) sulfate in sulfuric acid absorbs alkanes and reacts with them (83). The reaction taking place is unclear, but it is suggested that hydrogen abstraction from the alkane occurs as the first step and this is then followed by sulfonation or oxidation. Products of the reaction have not been given.

$$\begin{array}{c} \text{R}_3\text{C}-\text{H} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{O} \\ \quad \quad \quad \diagup \\ \text{HO}-\text{Cr}-\text{OH} \\ \quad \quad \quad \diagdown \\ \quad \quad \quad \text{O} \end{array} \longrightarrow \text{R}_3\text{C}-\text{OCr}(\text{OH})_3 \quad (21)$$

VI CONCLUSION

The contents of Sections II, III, and IV show that the activation of C—H bonds in alkanes by transition metal compounds has much in common with the activation of C—H bonds in aromatic compounds. It appears, therefore, to be more profitable at the present time to draw mechanistic parallels between alkanes and aromatic systems, as has been done here, than, say, between alkanes and molecular hydrogen, although, of course, much work has been done on hydrogen activation (39).

Although it is clear that alkane activation is possible, the work done so far using soft metals as catalyst has not produced a reaction that converts alkanes into useful products. Nor does it point very clearly in the direction where progress will be made. It may be that studies on dimeric and cluster compounds, on polyhydrides, or on transition metal alkyls will indicate the paths to be explored. The work using hard catalysts is at present very limited and can be expected to be developed much further in future years.

Alkane activation remains one of the most worthwhile challenges to the ingenuity and imagination of the organometallic chemist.

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Supported Transition Metal Complexes as Catalysts

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I

INTRODUCTION

In an energy conscious world it is perhaps fitting to start any discussion of catalysis by emphasizing that chemists have long been interested in ways of minimizing the energy requirements of chemical reactions and to this end have diligently sought out suitable catalysts. The word "catalysis" was first used by Berzelius in 1836 to describe a number of previous experimental observations including Thenard's (1813) that ammonia was decomposed by metals and Dobereiner's (1825) that the presence of manganese dioxide modifies the rate of decomposition of potassium chlorate.

For many years, most of the intentionally used catalysts (as compared to those accidentally introduced) were heterogeneous and in which reaction was promoted by adsorption of some or all of the reactants on the catalyst surface. As the name suggests, heterogeneous catalysis is at least a two-phase process generally involving a solid catalyst. Heterogeneous catalysts may be thought of as the first generation of catalysts. More recently, homogeneous catalysts (second-generation catalysts) have been developed in which a specific chemical compound is introduced into the reaction as a molecular entity. Such catalysts normally operate in solution and the catalyst is dissolved in the reaction mixture. Catalysis occurs through the formation of intermediate compounds. As with all classification schemes, although many examples of catalysis are clearly either heterogeneous or homogeneous, there are many that lie close to the borderline and in which it is uncertain whether the true catalyst for the reaction is a heterogeneous or a homogeneous one.

In order to appreciate the reasons for the present interest in supported complex catalysts, which may be called the *third-generation* catalysts, it is useful to look at the advantages and disadvantages of the heterogeneous and homogeneous catalysts under a number of headings.

1. Separation of the catalyst. The major disadvantage of homogeneous catalysts is the problem of separating the very expensive catalyst from the products at the end of the reaction. With heterogeneous catalysts this can be achieved by some kind of coarse filtration, whereas with homogeneous catalysts a very efficient distillation or ion-exchange process is usually required. Distillation is inevitably an endothermic process and is, therefore, expensive. Unless it is efficient, it will result in small catalyst losses which may (a) render the process uneconomic and/or (b) contaminate the product, which, for example, in the case of a foodstuff, would be unacceptable. It should be pointed out that two of the commercially successful homogeneously catalyzed processes, namely the Wacker process for oxidation of ethylene to acetaldehyde (105) and the Monsanto process for the carbonylation of methanol to yield acetic acid (101), depend in part for their success on the relatively low boiling points of the products (acetaldehyde, 20.8°C and acetic acid, 117.9°C). Of course, in some cases, such as the hydrogenation of soft oils to yield components suitable for incorporation into margarine, the products decompose before their boiling points (even under reduced pressure) so that distillation is not a practical method for separation of the catalyst in such cases. Distillation is also impossible in the case of reactions giving high-boiling side products that would steadily build up in concentration if they were not removed.

2. Efficiency. In a heterogeneous system, the catalytic reaction must

necessarily take place on the surface of the catalyst so that all atoms or molecules of the catalyst not present at the surface remain unused. By contrast, all the molecules in a homogeneous catalyst are theoretically available as catalytic centers so that these catalysts are potentially more efficient in terms of the amount of catalyst needed to catalyze a given amount of reaction.

3. Reproducibility. Homogeneous catalysts have the advantage over heterogeneous catalysts of being totally reproducible because they have a definite stoichiometry and structure. By contrast, the structure of the surface of a heterogeneous catalyst is heavily dependent on both its method of preparation and its history subsequent to preparation.

4. Specificity. A given homogeneous catalyst will generally have only one type of active site and, therefore, will often be more specific than a heterogeneous catalyst where several types of active site may be present in the form of different surface defects. These defects are extremely difficult to control. The specificity of a homogeneous catalyst can often be selectively modified by altering the other ligands present in such a way as to alter either the electronic nature or the steric requirements of the site.

5. Controllability. Closely related to specificity is the fact that, because a homogeneous catalyst has a definite structure, it can be much more easily modified in order to control a reaction. Thus, when the homogeneous catalyst $[\text{Rh}(\text{acac})(\text{CO})_2]$ is altered to $[\text{Rh}(\text{acac})(\text{CO})(\text{PPh}_3)]$, the ratio of normal to branched aldehydes obtained when 1-hexene is hydroformylated is altered from 1.2:1 to 2.9:1 (4).

6. Thermal stability. The thermal stability of heterogeneous catalysts, such as pure metals and metal oxides, is often much higher than that of homogeneous catalysts. Since the rate of most reactions increases with temperature, a high operating temperature may be an advantage. It should be noted that high temperatures are not always ideal because some reactions involve a preequilibrium step that may be disfavored by increasing the temperature. This is particularly true of reactions involving olefins: a recent survey (47) has shown that the entropy change on metal-olefin complex formation is almost invariably negative so that the stability of metal-olefin complexes decreases with increasing temperature.

7. Solvent. Whereas the range of suitable solvents for a homogeneous catalyst is often limited by the solubility characteristics of the catalyst, this clearly presents no problem for a heterogeneous catalyst.

At first sight it might appear that the balance of the advantages and disadvantages of these two types of catalyst would lie with the homogeneous catalysts. However this is not so. The problem of catalyst

separation is so important that, apart from one or two rather notable exceptions, chemical processes based on homogeneous catalysts are very rare. Recently, considerable research effort has been expended in developing catalysts that combine as many as possible of the advantages of each of the two extreme types. In this work there have been two major approaches.

1. Fluid-bed catalysts. The use of fluid-bed catalysts represents an attempt to homogenize heterogeneous catalysts. We shall not pursue this area here: the interested reader is referred to Flood and Lee (32) for an introductory article to this field.

2. Supported complex catalysts. These catalysts, which form the subject of the present review, essentially involve a compound of a metal covalently bound to some form of support. For example, a very valuable homogeneous hydrogenation catalyst is the Wilkinson catalyst $[(PPh_3)_3RhCl]$. Supported Wilkinson catalysts have been prepared by replacing one of the triphenylphosphine ligands by polystyrene- $C_6H_4CH_2PPh_2$ (37). In this way the rhodium(I) complex is bound on to an insoluble polymer.

Although a number of biochemical studies have been reported in the last decade or so in which enzymes bound to organic polymers or glass supports have been studied (80), the idea of binding homogeneous catalysts to solid-phase supports is more recent, the first published work being by Haag and Whitehurst (40-43) who used sulfonated cross-linked polystyrene resins in which the metal complex (e.g., $[Pt(NH_3)_4]^{2+}$) was ionically bound to the resin. Subsequently, cross-linked polystyrene resins with amino (23) and phosphino (21, 25) substituents have been used to bind the metal complex covalently. In addition to ionic and covalent links, van der Waals forces can provide the link, as in catalysts in which $[(PhCN)_2PdCl_2]$ (116), $RhCl_3$ in ethylene glycol (1), or $[(PPh_3)_2Rh(CO)Cl]$ in butyl benzyl phthalate (99) are sorbed onto silica gel and other supports (100). Such supported complexes have, of course, been used for some time in the GLC separation of olefins.

The original objective in binding metal complexes to insoluble supports was undoubtedly to get over the solubility problems of homogeneous catalysts which made their separation after reaction such a problem. However, there have been other "spin-off" advantages. In particular the selectivity of the supported catalysts is often greater than their homogeneous counterparts because, in addition to the electronic and steric selectivity present in the free complex, further selectivity arises because the solvent channel leading up to the active site has both a size restriction and polar properties. This results in the diffusion rate of two

substrates to the active site being dependent on both their relative molecular sizes and their relative polarities. Further selectivity, analogous to that present in enzymes, is introduced by the groups in the polymer around the active site. These groups, which are a consequence of the three-dimensional nature of the polymer, have no counterpart in homogeneous catalysts. Moreover, these groups may prevent, or at least reduce, the ability of poisons to destroy the catalytic activity. We may thus expect, in favorable cases, to find supported complex catalysts of greater selectivity than their homogeneous counterparts, and it should be remembered that these, in turn, are often more selective than the heterogeneous catalysts. Thus, since they are inevitably going to be expensive, we may expect in the future to see supported complex catalysts used in reactions for which high selectivity is important and this will generally involve more complex substrates such as are encountered in the pharmaceutical and dyestuffs industries.

II

PREPARATION OF SUPPORTED COMPLEX CATALYSTS

A. *Preparation of the Support*

A number of materials have been used as the basic support (Table I). Although it is convenient to describe them as either inorganic or organic supports, there is, as with most classification schemes, a considerable

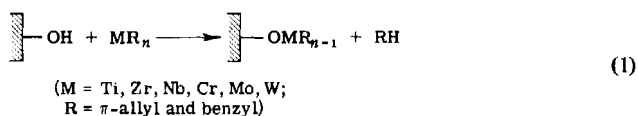
TABLE I
MATERIALS USED TO SUPPORT METAL COMPLEXES

Inorganic	Organic
Silica	Polystyrene
Zeolites	Polyamines
Glass	Silicates
Clay	Polyvinyls
Metal oxides such as alumina	Polyallyls
	Polybutadiene
	Polyamino acids
	Urethanes
	Acrylic polymers
	Cellulose
	Cross-linked dextrans
	Agarose

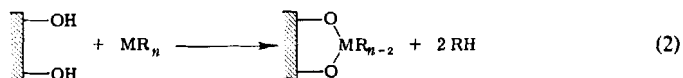
region of overlap particularly in the silicate region. Undoubtedly, the most important of these materials at present are silica and polystyrene and the techniques used to make these suitable as supports are generally typical of those required for inorganic and organic supports respectively.

1. Silica

On the surface of silica are silanol groups (—Si—OH) that can be used to bind metal complexes, either directly or through an intermediate group. Thus, direct reaction,

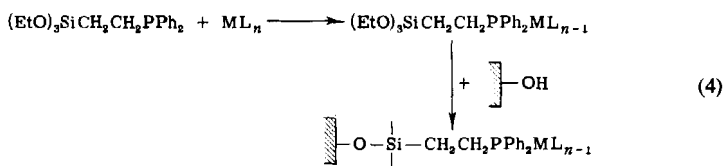
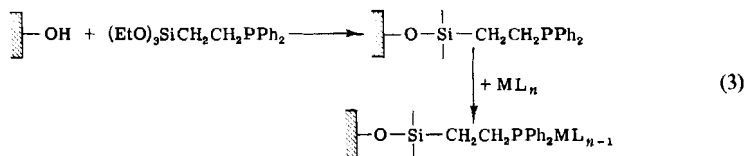


has been used to bind moisture-sensitive organometallic complexes to silica (19). Clearly, there is a possibility, if the surface silanol groups are in the correct stereochemical arrangement, of chelate formation,



as has been detected by ESR when $[\text{Nb}(\pi\text{-allyl})_4]$ was the metal complex.

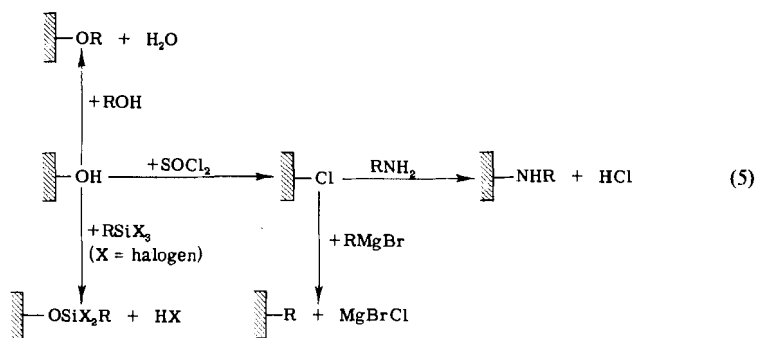
Several research groups have concentrated on attaching metal complexes to silica by introducing phosphine groups on to the surface. They have used two approaches that differ only in the order of the steps (2, 4, 5, 87):



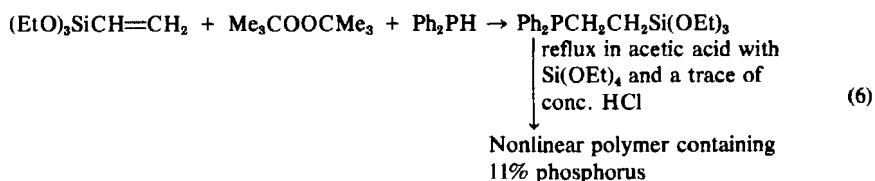
The advantages of the first route [Eq. (3)] are (i) the range of bridging groups can readily be varied, for example, to $-\text{CH}_2\text{CH}_2\text{CH}_2\text{PPh}_2$ or $4-(\text{CH}_2)_4\text{C}_5\text{H}_4\text{N}$; (ii) metal complexes that are unstable in solution, for example because they readily dimerize or are coordinatively unsaturated, may be prepared because the rigidity of the surface prevents molecular interactions; (iii) the surface of the silica after reaction with the bridging group will still be very polar due to unreacted silanol groups (these, however, can be removed by subsequent silylation, thus decreasing the polarity of the surface). In this way the microenvironment of the catalytic center can be carefully controlled, as it is, of course, in a metalloenzyme, with consequent advantages in terms of the activity and selectivity of the catalyst.

The main disadvantage of reaction (3) is the difficulty of determining the precise nature of the catalytic site since this is formed in the support. Reaction (4) was designed to obviate this problem since, in principle, the complex is isolated and may be characterized by standard methods. In practice, however, many complexes of this type cannot be isolated as crystalline solids but only as oils that must be purified chromatographically using nonhydroxylic phases.

Although reactions (1)–(4) are the only reactions that appear to have been used in preparing supported metal catalysts, there are several other ways that could be used, for example,



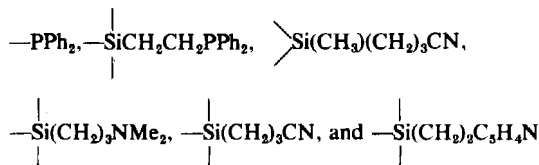
All of these reactions have been used to bind organofunctional groups to inorganic surfaces for chromatographic purposes (18, 48, 61, 68, 69). A totally different approach to the use of silica as the support is illustrated in the following reaction in which the functional group, for example, a tertiary phosphine, is built into the trialkoxysilane which is then polymerized to produce a nonlinear polymer based on an $-\text{Si}-\text{O}-\text{Si}-$ backbone (115):



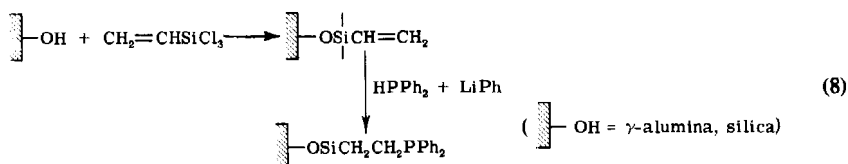
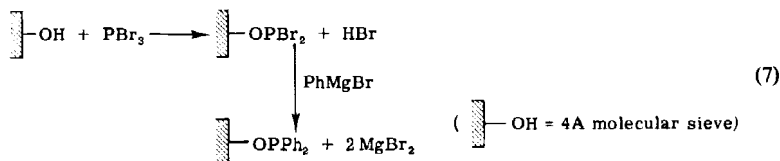
Reaction (6) demonstrates the limitation of classifying supports as organic or inorganic since it involves an inorganic support prepared from an organic reagent.

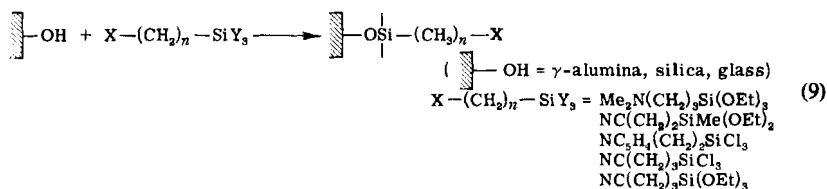
2. Other Inorganic Supports

Inorganic materials, such as γ -alumina, molecular sieves (zeolites), and glass, although being essentially metal oxides, have hydroxyl groups on the surface that can be used as the point of attachment. Capka (20) has pioneered the use of these materials by attaching groups, such as



to the surface by means of the following reactions:





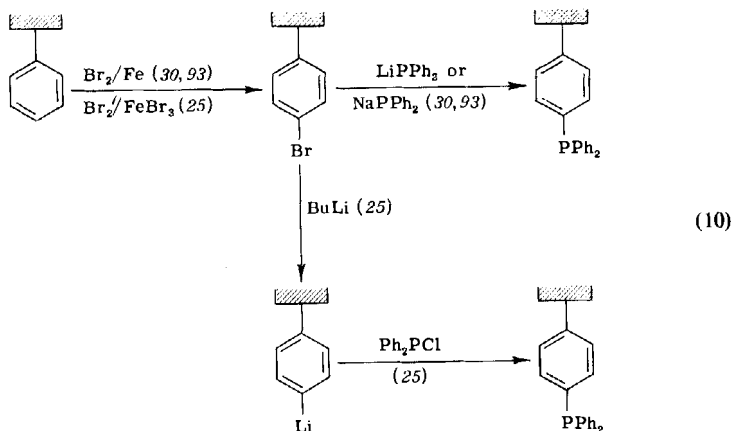
In addition, moisture-sensitive organometallics have been introduced directly onto alumina using reactions exactly analogous to Eqs. (1) and (2) (19).

3. Polystyrene

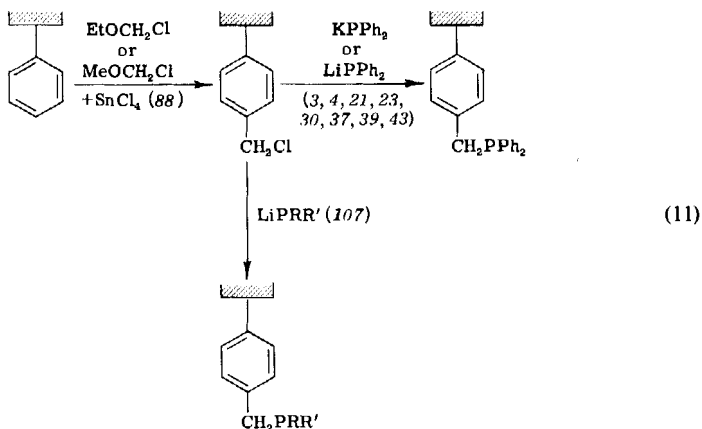
Polystyrene cross-linked with a proportion of divinylbenzene has been widely used as a support with a range of functional groups (or none at all) to bind the metal to the polymer. Some authors have prepared their own polymer from monomer but many have used commercially produced cross-linked polystyrene beads. If these are used, it is essential that they are pretreated so as to remove the impurities that remain on the surface after the emulsion polymerization reactions used to produce them (97). The commonest impurities remaining after emulsion polymerization are hydrated colloidal alumina, fullers' earth, carboxymethyl cellulose, stearic acid, sodium lauryl sulfate, and sodium polyacrylamide (106), and, if they are left on the surface, they result in the formation of surface ions that prevent penetration of ionic reagents such as butyl lithium or lithium diphenylphosphide. A satisfactory procedure for removing the surface impurities involves successive washings in 1 *N* NaOH (60°C), 1 *N* HCl (60°C), 1 *N* NaOH (60°C), 1 *N* HCl (60°C), H₂O (25°C), DMF (40°C), 1 *N* HCl (60°C), H₂O (60°C), CH₃OH (20°C), 3:2 (v/v) CH₃OH:CH₂Cl₂, 1:3 (v/v) CH₃OH:CH₂Cl₂, 1:9 (v/v) CH₃OH:CH₂Cl₂, pure CH₂Cl₂, followed by drying to constant weight at 100°C *in vacuo* (10 torr overnight, then 0.1 torr for several hours).

a. Phosphinated Polystyrenes. Three main starting materials, styrene, *p*-bromostyrene, and *p*-diphenylphosphinostyrene, have been used to prepare phosphinated polystyrenes. Each of the monomers is first polymerized in the presence of divinylbenzene to introduce cross-linking. Starting from polystyrene itself, two main phosphination routes

have been used, one yielding —PPh_2 and the other $\text{—CH}_2\text{PPh}_2$ groups:

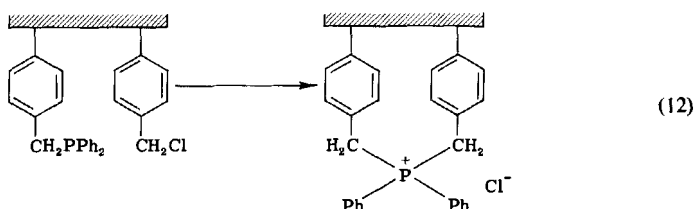


In each case it appears that the same end product can be obtained by several routes. However, the end products are not exactly identical because the reactivities of the various reagents with the polymer differ so that the number and distribution of the phosphine groups differ. The chloromethylated polystyrene produced in the first stage of the reaction,



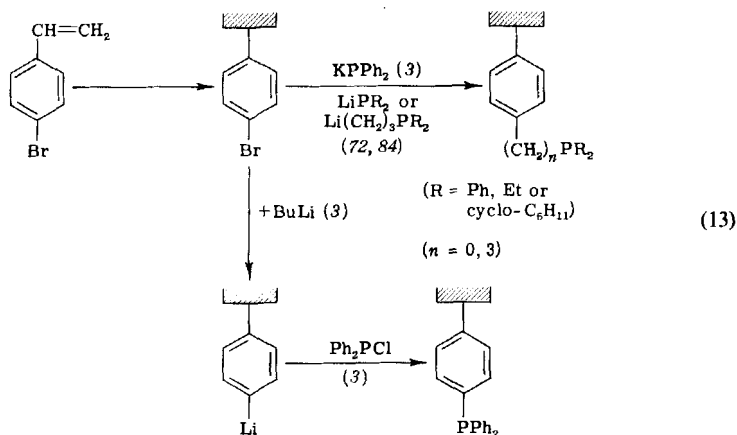
is often known as Merrifield's resin following its extensive use by this author in the synthesis of peptides (73). Merrifield showed that the chloromethyl groups are distributed right throughout the polymer, a large proportion being "inside" the polymer (74). The introduction of the group $\text{—CH}_2\text{PPR}'$, where $\text{R} = \text{phenyl}$ and $\text{R}' = \text{methyl or menthyl}$, enables optical activity to be introduced into the polymeric support

(107). One of the difficulties with $-\text{CH}_2\text{PPh}_2$ groups is that they can interact with neighboring chloromethyl groups leading to quaternization:

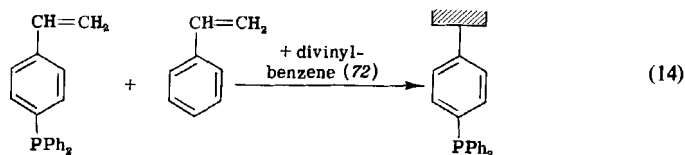


The resulting phosphonium complexes yield very poor rhodium(I) hydroformylation catalysts (77).

In reaction (10), poly-*p*-bromostyrene was prepared by the bromination of polystyrene. However, this may also be synthesized by polymerizing *p*-bromostyrene in the presence of divinylbenzene using benzoyl peroxide as the polymerization initiator. The subsequent treatments are essentially similar to those in reaction (10), for example,



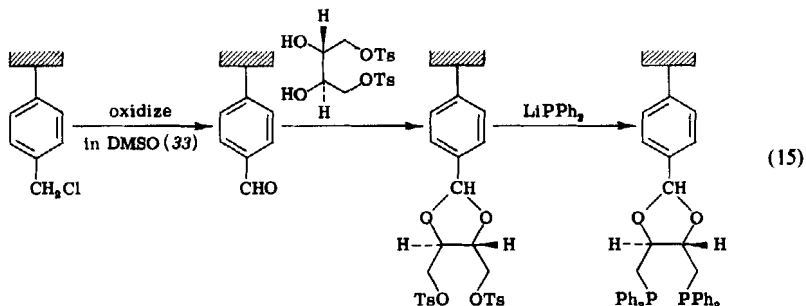
Similarly, poly-*p*-diphenylphosphinostyrene has been prepared by polymerizing the monomeric material with styrene and divinylbenzene:



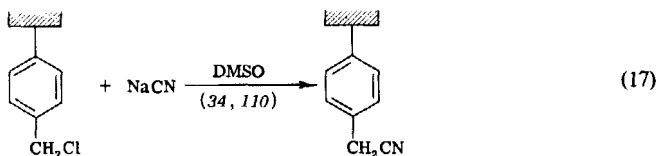
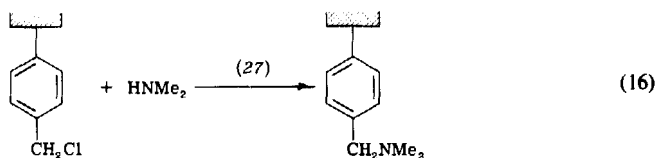
Each of the polymeric supports have different numbers and arrangements of the diphenylphosphine groups in the polymer. At present the

main method for distinguishing them has been elemental analysis to determine the phosphorus content. Obviously, this does not give any indication of the arrangements of the groups with the polymers.

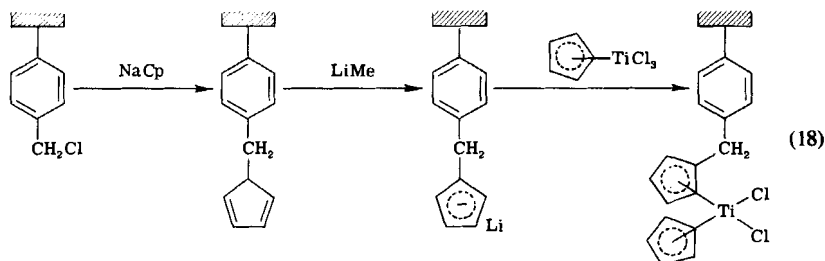
An optically active, supported chelating diphosphine has been prepared from the Merrifield resin using reaction (15) to give a polymer-supported analog of the homogeneous diop catalysts (28, 94).



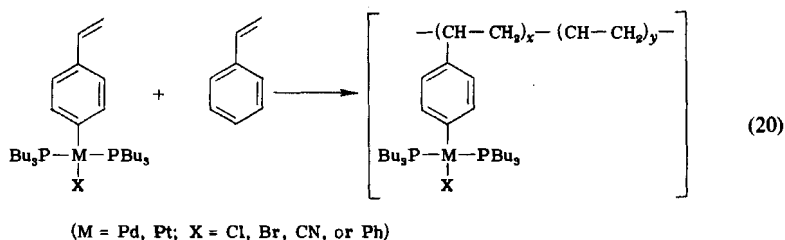
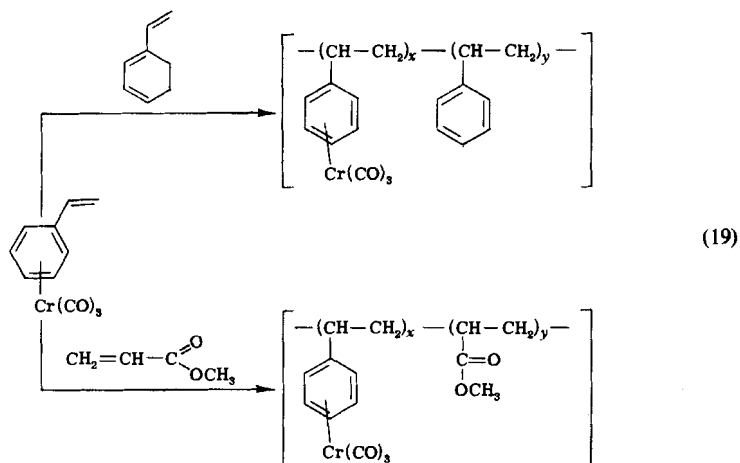
b. Other Groups on Polystyrene. Polystyrene resins with a range of substituents other than tertiary phosphines have been used as supports. The simplest of these are the commercial ion-exchange resins containing sulfonate groups (40–43), used for cationic complexes, such as $[\text{Pd}(\text{NH}_3)_4]^{2+}$, and quaternary ammonium groups (66) that are used for anionic complexes such as $[\text{PdCl}_4]^{2-}$. In addition, styrenes substituted in the para position with tertiary amino [$-(\text{CH}_2)_n\text{NMe}_2$, $n = 0, 1, 2$] (23, 27, 57, 75, 98), cyanomethyl (23, 63, 64, 98), and thiol groups (45, 98) have been prepared:



Titanocene dichloride has been built onto a polystyrene support by first introducing cyclopentadienyl methyl groups into the polymer and then reacting these with cyclopentadienyltitanium trichloride (36):



c. Catalysts with Direct Metal–Polystyrene Links. Two groups, one in the United States (89, 90) and the other in Japan (35), have prepared complexes in which styrene is coordinated to a metal. This styrene is then copolymerized either with further styrene or with methylacrylate:



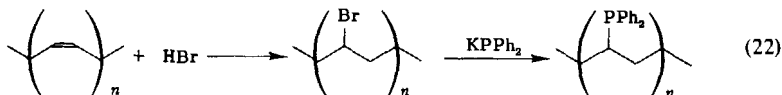
4. Other Organic Supports

A considerable number of organic supports other than polystyrene have been used. They can be conveniently divided into two groups. The

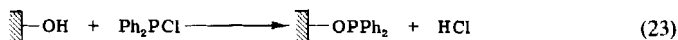
first require modification to introduce a suitable ligand donor atom, which is usually a phosphine. These include polyvinyl chloride (3),



polybutadiene (3),



polyvinyl alcohol (3) and cellulose (95),



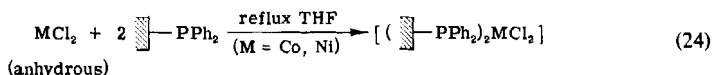
The second group already contains donor groups (usually oxygen or nitrogen) and, thus, requires no further chemical modification. These include polyacrylic acid (82, 83), polyvinyl alcohol (60), polymeric Schiff's bases (65), poly-L-methylethylenimine (52), poly-2-vinylpyridine (78, 79, 98), poly-4-vinylpyridine (24), and polyvinylamine (54, 59).

B. Introduction of Metal onto Support

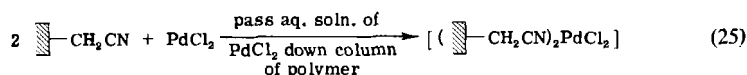
A number of examples of the introduction of the metal onto the support have already been mentioned in the previous section either because one of the ligands coordinated to the metal became part of the polymer [see reactions (4) and (18)–(20)] or because the metal complex reacted directly with the support [reactions (1) and (2)] or because the preparation simply involved sorption by van der Waals forces onto the support (Section I). In the present section, we shall be particularly concerned to introduce metal complexes onto polymeric supports that have typical donor groups such as tertiary phosphine and amine. A number of routes, most of which are of fairly general applicability, have been used.

1. Direct Reaction of Metal Halide with Support

The direct reaction of a metal halide has been used to introduce cobalt(II) and nickel(II) onto polymeric phosphine supports (3),



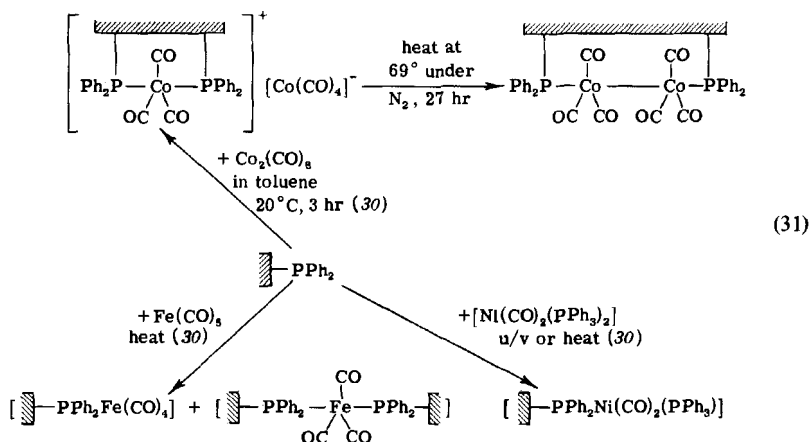
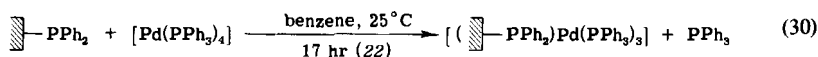
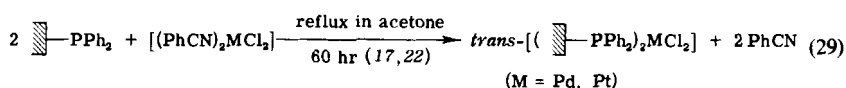
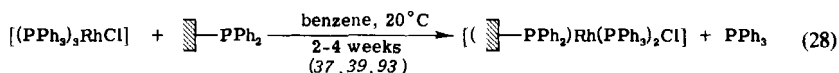
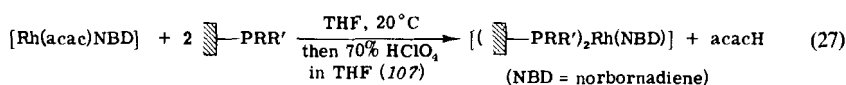
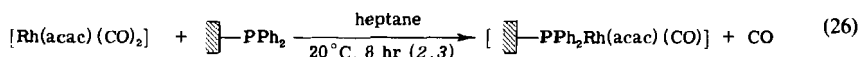
rhodium(III) onto polymeric amine supports (23), and palladium(II) onto nitrile supports (64),



The conditions are essentially those that would have been used had the ligands been simple rather than polymeric.

2. Displacement of a Ligand from Metal

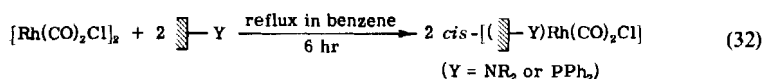
By far the commonest route for preparing supported complex catalysts is to displace a ligand already coordinated to the metal complex by a ligand from the polymer. Some examples of this are given in reactions (26)–(31).



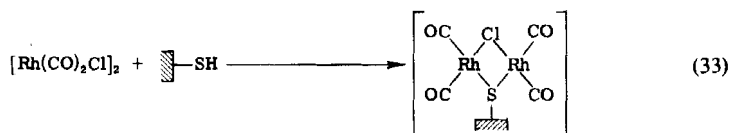
It should be appreciated that some of the products are idealized in that the reactivities of donor groups vary according to their position within the polymer. Thus, for example, where chelation is shown not every metal atom may be chelated.

3. Bridge Splitting

Chloro-bridged dimeric rhodium(I) complexes, such as $[\text{Rh}(\text{CO})_2\text{Cl}]_2$ (27, 57, 98) and $[\text{Rh}(\text{COD})\text{Cl}]_2$ (25), react with polymeric resins to give monomeric polymer-bound complexes with phosphine and amine supports.



However, with thiol supports, the bridge is not split, the thiol group being deprotonated and then binding in the bridge position (98):



Although, at present, bridge-splitting reactions have only been used in the preparation of rhodium(I)-supported catalysts, they clearly have further potential and are likely to be used for other d^8 metal complexes in the future.

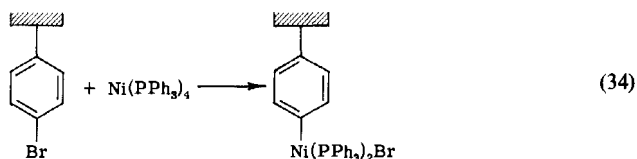
4. Reductive Reaction with a Support

Reaction of a metal complex with a support accompanied by reduction of the metal to a lower oxidation state has been used to prepare supported rhodium(II) and platinum(II) catalysts. Thus, $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ reacts with polyacrylic acid under reflux in alkaline methanol to yield a rhodium(II) species (82) analogous to rhodium(II) acetate (56). An active platinum(II) (82) hydrosilylation catalyst can be prepared by treating a styrene-divinylbenzene copolymer bearing $-\text{CH}_2\text{NMe}_2$ groups with $[(\text{PhCH}_2)\text{Me}_2\text{NH}]_2^+[\text{PtCl}_6]^{2-}$ and reducing the platinum(IV) to a mixture of platinum(II) (active) and platinum metal (inactive) by exposure to acetylene (75). It is very probable that treatment of phosphinated polymers with rhodium(III) chloride in ethanol yields a rhodium(I)-supported catalyst (21) since the reaction is analogous to that used to prepare the homogeneous Wilkinson catalyst (86). However, the

actual oxidation state of the supported rhodium has not been determined.

5. Oxidative Addition of Support to Metal Complex

Nickel(II) catalysts with a direct nickel(II)–polystyrene bond have been prepared by oxidative addition of tetrakis(triphenylphosphine) nickel(0) to brominated polystyrene (58):



In view of the importance and widespread occurrence of oxidative addition reactions in organometallic chemistry, this type of reaction clearly has much potential for future use.

III

REACTIONS CATALYZED BY SUPPORTED CATALYSTS

A number of reactions, principally of olefinic substrates, that can be catalyzed by supported complexes have been studied. These include hydrogenation, hydrosilylation, hydroformylation, polymerization, oxidative hydrolysis, acetoxylation, and carbonylation. Each of these will be considered in turn together with the possibility of carrying out several reactions consecutively using a catalyst containing more than one kind of metal complex.

A. Hydrogenation

Table II summarizes the systems that have been studied as hydrogenation catalysts. The majority of these involve d^8 metal complexes mainly rhodium(I), palladium(II), and platinum(II), which have been found to be the most successful of the homogeneous hydrogenation catalysts.

In order to determine the optimum catalyst for a particular hydrogenation reaction, there are a number of parameters that can be varied.

TABLE II
HYDROGENATIONS CATALYZED BY SUPPORTED METAL COMPLEXES

Metal complex	Polymer	Substrate	References
RhCl_3	Cross-linked polystyrene-substituted with — CH_2PPh_2 and — CH_2NMe_2 ; polymethylacrylate with — $\text{O}(\text{CH}_2)_2\text{NMe}_2$ and — $\text{O}(\text{CH}_2)_2\text{CN}$	<i>n</i> -Heptene	23
$[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$	Phosphinated 2% cross-linked polystyrene	Cyclohexene 1-Hexene Δ^2 -Cholestene Octadecene Cyclooctene Cyclododecene	37
$[\text{Rh}(\text{C}_2\text{H}_4)_2\text{Cl}]_2$	Phosphinated acetal of cross-linked styrene	α -Methylstyrene 2-Ethyl-1-hexene	28
RhCl_3 RhCl_3 then PPh_3 RhCl_3 then PHPh_2 RhCl_3 then C_2H_4 $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ $[\text{Rh}(\text{PHPh}_2)_3\text{Cl}]$	Phosphinated 2% cross-linked polystyrene	1-Heptene Crotonaldehyde Vinyl acetate Vinyl ethyl ether	21
$[\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$ $[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$	Phosphinated cross-linked polystyrene	—	25
PtCl_2	Nylon	Benzene	96

H ₂ PtCl ₆ PdCl ₂	1:1 Copolymer of 2,3-bis(diethylphosphine)- 1,3-butadiene and maleic anhydride	1-Hexyne Isoprene Phenyl acetylene	81
[Rh(C ₂ H ₄) ₂ Cl] ₂	Poly(<i>p</i> -diphenylphosphinostyrene)	—	70
K ₂ PdCl ₄	Amberlyst A27	Cyclohexene Styrene	66
[Rh(COD)Cl] ₂	Phosphinated Amberlite XAD-2	1-Hexene	4
NiCl ₂ then NaBH ₄ [Rh(acac)(CO) ₂] [Rh(COD)Cl] ₂ RhCl ₃	Phosphinated polyvinyl chloride	Propene 1-Hexene 1-Octene	3,15
[Ir(COD)Cl] ₂	Phosphinated silica	1-Hexene Isoprene	5
[Rh(PPh ₃) ₃ (CO)H] RhCl ₃	Phosphinated silica and phosphinated Amberlite XAD-2	2-Pentene 1-Pentene 2-Methylbut-2-ene 2-Methylbut-1-ene Cyclohexene Cyclooctene	76
[(EtO) ₃ SiCH ₂ CH ₂ PPh ₂ Rh(acac)(CO)]	Silica	1-Hexene	2,4
Titanocene	Chloromethylated cross-linked polystyrene	1,3-Cyclooctadiene 1,5-Cyclooctadiene Styrene 3-Hexyne 1-Hexene	36

(continued)

TABLE II (Continued)

Metal complex	Polymer	Substrate	References
$\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$	Poly-1-methylethylenimine	Methyl acetoacetate	52
$[\text{Pt}(\text{1,5-COD})\text{Cl}_2]$	Amberlyst 15	2-Methoxypropanol	41
Nickel(II) hexanoate, Cu(II), Pd(II)	Poly(acrylic acid)	—	67
$[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ $[\text{Rh}(\text{MeCH}=\text{CH}_2)_2\text{Cl}]_2$	Phosphinated (10%) cross-linked (2%) polystyrene	—	38, 39
PtCl_2 PdCl_2	Phosphinated chloromethylated Amberlite XAD-4	Soybean methyl ester 2,4-Hexadiene 1,3-Hexadiene 1,5-Hexadiene Cyclohexene 1,3-Cyclohexadiene 1,4-Cyclohexadiene	16, 17

RhCl_3	Amberlite IRC-84	Styrene Maleic acid Mesityl oxide	83
$[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$ $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$	Phosphinated cross-linked polystyrene	4-Vinylcyclohexene 1,5-Cyclooctadiene 1,5,9-Cyclododecatriene	93
$[\text{Rh}(\text{acac})(\text{NBD})]$	Phosphinated cross-linked polystyrene	Acetone Methyl ethyl ketone Acetophenone 1-Hexene Cyclohexene	107
$[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$	Phosphinated cellulose	Methyl α -phthalimidoacrylate	95
$[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$	Silica gel, alumina, activated charcoal, diatomaceous earth	Propene	100
$[\text{Ir}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$	Phosphinated cross-linked polystyrene	4-Vinylcyclohexene	55

1. *Nature of the Support*

The nature of the support can have a very profound influence on the catalyst activity. Thus, phosphinated polyvinyl chloride supports are fairly inactive (15), and phosphinated polystyrene catalysts are considerably more active (37), but rather less active particularly when cyclic olefins are the substrates than phosphinated silica supports (76). Silica-supported catalysts may be more active because the rhodium(I) complexes are bound to the outside of the silica surface and are, therefore, more readily available to the reactants than in the polystyrene-based catalysts where the rhodium(I) complex may be deep inside the polymer beads. If this is so, the polystyrene-based catalysts should be more valuable when it is desired to hydrogenate selectively one olefin in a mixture of olefins, whereas the silica-based catalysts should be more valuable when a rapid hydrogenation of a pure substrate is required.

2. *Effect of Cross-Linking*

In the organic polymer supports, it is possible to vary considerably the degree of cross-linking present in the support. (In the polystyrene-based catalysts, this is usually achieved by varying the amount of divinylbenzene that forms the cross-links.) The influence of cross-linking can be very profound: for example, using phosphinated polystyrene catalysts based on $[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$, Grubbs (37, 39) found that the supported catalyst was only 0.06 times as active as the homogeneous catalyst. His polymer was 2% cross-linked and fairly large beads were used (74–149 μm diameter). By contrast, using smaller (37–74 μm diameter) beads of lower (1%) cross-linking, Pittman (93) found the supported catalyst was 0.8 times as active as the homogeneous catalyst—an improvement by a factor of 13. In addition to altering the activity, varying the degree of cross-linking alters the specificity: the greater the cross-linking, the tighter the polymer chains are bound and, hence, the more difficult it becomes for any but the smallest substrate molecules to enter the polymer. Thus, the rates of hydrogenation of a series of olefins in benzene, using 100–200 mesh, 2% cross-linked polystyrene, were found to decrease in the order (39):



A first attempt to calculate the effective pore size within the polymer from the substrate selectivity has not been oversuccessful, since calculated pore sizes of about 7 Å were obtained in polymers with measured pore sizes in the region of 150 to 200 Å. Although, of course, the

substrate will be solvated and, hence, appear larger than the simple molecule, this is unlikely to account for the discrepancy completely.

3. Nature of the Solvent

It has been well-established that solvent polarity affects the swelling of polymers. For polystyrene an increase in solvent polarity decreases the swelling of the polymer. When this was investigated the simple relationship predicted did not obtain because, in addition to the change in pore size, an increase in polarity leads to an increase in the polar gradient between the bulk solvent and the local environment of the catalytic site that promotes diffusion of nonpolar olefins to the catalytic site but impedes diffusion of polar olefins (39). Accordingly, the complex catalyst selectivity shown in Fig. 1 is observed. Nonpolar olefins all show initial rate enhancement as the percentage of ethanol is increased until, at high concentrations, the pore size decreases and size effects again become important. Polar olefins show steady rate reduction with increasing solvent polarity. Clearly, the influence of solvent is an important factor that can be varied in order to control the activity and selectivity of a particular supported catalyst.

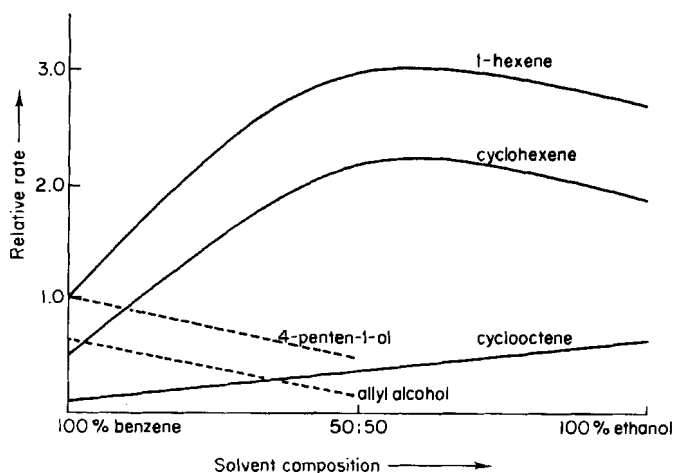
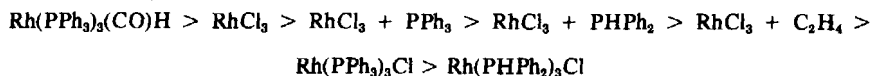


FIG. 1. Influence of solvent polarity on the relative rates of hydrogenation of nonpolar (—) and polar (---) olefins. (Reproduced by permission from the *Journal of Macromolecular Science*).

4. Nature of the Metal Complex

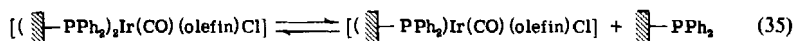
The nature of the metal complex can have a profound influence on the rate of hydrogenation, and, even in cases where similar complexes have been prepared by different routes, considerable differences in reactivities can be observed. Thus, the effectiveness of rhodium(I) complexes on phosphinated polystyrene decreases in the order, (21, 76):



5. Activity of Supported vs. Homogeneous Catalysts

Although supported catalysts have advantages of selectivity with respect to substrate and ease of separation of the catalyst after reaction, as compared to homogeneous catalysts, most industrialists still tend to ask about the relative activities of the two types of catalyst. At present the supported catalyst are generally less active than the homogeneous, although they can approach 80% activity (93). The lower activity of the supported catalysts reflects the fact that some of the metal centers are bound in substrate-inaccessible sites within the pores of the catalyst; accordingly, the less of these sites there are, as in silica, the greater is the activity.

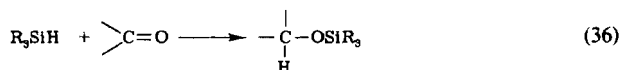
A special situation arises if the active homogeneous catalyst readily dimerizes, because once the monomeric units have been bound to the support dimerization is prevented. Thus, titanocene is a reactive intermediate in the reduction of olefins by mixtures of $[\text{Cp}_2\text{TiCl}_2]$ and phenylmagnesium bromide (109), but it is rapidly converted into an inactive dimeric compound (10). However, when $[\text{Cp}_2\text{TiCl}_2]$ was bound to a polymeric support, as in reaction (18), it gave, on treatment with butyl lithium, a catalyst that was 6.7 times more active as a homogeneous hydrogenation catalyst than unsupported $[\text{Cp}_2\text{TiCl}_2]$ also treated with butyl lithium (36). The greater reactivity of the supported catalyst was ascribed to the prevention of dimerization, a suggestion that was partly based on ESR evidence. Polymer-bound $[(\text{---PPh}_2)_2\text{Ir}(\text{CO})\text{Cl}]$ was found to be more active as a hydrogenation catalyst for 4-vinylcyclohexene than its homogeneous counterpart because the equilibrium,



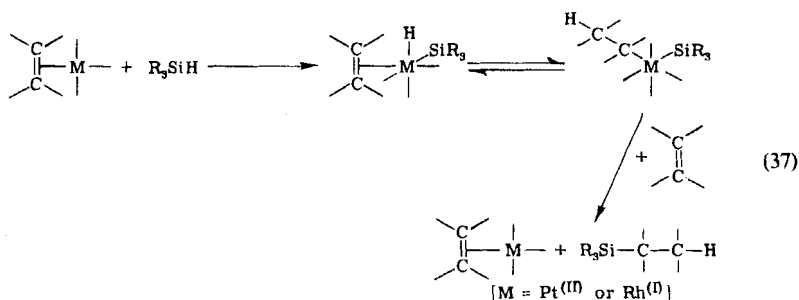
lies further to the right for the polymeric phosphine than for triphenylphosphine owing to steric constraints within the polymer that retard the reverse reaction (55).

B. Hydrosilylation

Hydrosilylation is formally the addition of the units of R_3Si and H (R may be alkyl, alkoxy, or halide) to an unsaturated group such as an olefin, acetylene, or ketone, e.g.,



The reaction is formally and mechanistically rather similar to hydrogenation. The principal catalysts that have been used in the homogeneously catalyzed reaction have been chloroplatinic acid [which is reduced to platinum(II)] and rhodium(I) complexes such as Wilkinson's complex $[Rh(PPh_3)_3Cl]$. Their mode of action probably involves oxidative addition of $H-SiR_3$ to give a platinum(IV) (46) or rhodium(III) (85) intermediate which then transfers the H and SiR_3 groups to the originally unsaturated bond:



A similar mechanism almost certainly takes place on polymer-supported complexes. Indeed, some evidence has been put forward for the formation of some platinum(II) species when a styrene/divinylbenzene copolymer bearing dimethylamino groups is treated with chloroplatinic acid (75).

Table III gives details of the use of supported catalysts in hydrosilylation reactions. There are, in principle, three ways in which the supported catalyst could act: (i) the reaction could take place at the metal site which itself remains bonded to the surface throughout the reaction; (ii) the catalytically active species or its precursor may be abstracted from the support into the solution by a reversible process so that the catalysis is effectively a homogeneous process; (iii) a possible mode of action essentially the same as the second except that the abstraction is irreversible. The fact that most of the catalysts can be reused several times and, indeed, that their catalytic activity increases slightly after the

TABLE III
HYDROSILYLATIONS CATALYZED BY SUPPORTED METAL CATALYSTS

Metal complex	Polymer	Substrates	References
H_2PtCl_6	Cross-linked polystyrene substituted with cyanomethyl groups	Acetylene with $HSiCl_3$	63, 75
$RhCl_3$	Cross-linked polystyrene substituted with $-CH_2PPh_2$, $-CH_2NMe_2$, or $-CH_2CN$ Polymethacrylate substituted with $-O(CH_2)_2CN$, $-OC_6H_4PPh_2$, $-O(CH_2)_3PPh_2$, or $-O(CH_2)_2NMe_2$ Amberlyst A21 Allyl chloride-divinylbenzene copolymer substituted with $-CH_2PPh_2$	1-Hexene or 1-heptene with $HSi(OEt)_3$, $HSiEt_3$, or $HSiCl_3$	23
$[Rh(C_2H_4)_2Cl]_2$	Phosphinated acetal of a cross-linked polystyrene	Acetophenone with Ph_2SiH_2	94
Na_2PdCl_4	Phosphinated silica [prepared by reaction (6)]	Allyl chloride or butadiene with $HSiCl_3$	115
$[Rh(C_2H_4)_2Cl]_2$	Phosphinated acetal of cross-linked polystyrene	Acetophenone or isobutyrophenone with various mono- and dihydrosilanes	28
$RhCl_3$ $RhCl_3$ followed by C_2H_4	Phosphinated 20% cross-linked polystyrene	1-Hexene, vinyl ethyl ether, acrylonitrile, or <i>trans</i> -2-heptene with $HSi(OEt)_3$	21

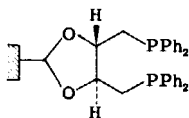
$[\text{Rh}(\text{CO})_2\text{Cl}_2]$	Dimethylaminomethylated cross-linked polystyrene	1-Heptene or styrene with HSiCl_3 Styrene, butadiene, 1-heptene-3,3-dimethyl-1-butene or 1-heptene-4,4-dimethyl-1-pentene with HSiEt_3	27
$[\text{Pd}(\text{PPh}_3)_3]$ $[\text{Pd}(\text{PPh}_3)_2\text{Cl}_2]$ $[\text{Pd}(\text{PhCN})_2\text{Cl}_2]$ $[\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}]_2$ PdCl_2	Cross-linked polystyrene containing $-\text{CH}_2\text{PPh}_2$ or $-\text{CH}_2\text{CN}$ Amberlyst A21	Butadiene with Me_3SiOH	22
$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	Poly(<i>p</i> -chloromethylstyrene)	2-Hexene	7
PdCl_2 RhCl_3 H_2PtCl_6	γ -Alumina, silica, molecular sieves, or glass with one of the following groups: $-\text{PPh}_2$, $\equiv\text{Si}(\text{CH}_2)_2\text{PPh}_2$, $\equiv\text{Si}(\text{Me})(\text{CH}_2)_3\text{CN}$, $\equiv\text{Si}(\text{CH}_2)_3\text{NMe}_2$, $\equiv\text{Si}(\text{CH}_2)_3\text{CN}$, or $\equiv\text{Si}(\text{CH}_2)_3\text{C}_5\text{H}_4\text{N}$	Butadiene, 1-heptene, 1-hexene, 1-decene, vinyl ethyl ether, or styrene with HSiCl_3 , HSiEt_3 , or $\text{HSi}(\text{OEt})_3$	20
$\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$	Phosphinated cross-linked polystyrene	Vinyl acetate with $\text{HSi}(\text{OEt})_3$	9
$[\text{Pd}(\pi\text{-C}_3\text{H}_5)\text{Cl}]_2$ $[(\text{PhCN})_2\text{PdCl}_2]$ $[(\text{PPh}_3)_2\text{PdCl}_2]$ $[(\text{PPh}_3)_2\text{PdBr}_2]$ $[\{\sigma\text{-C}_6\text{H}_4(\text{CH}_2\text{CN})_2\}\text{PdCl}_2]$	Cross-linked polystyrene with $-\text{CH}_2\text{PPh}_2$ or $-\text{CH}_2\text{CN}$ groups	Butadiene, isoprene, piperylene, chloroprene, or 2,3-dimethyl-1,3-butadiene with HSiCl_3 , HSiMeCl_2 , HSiEtCl_2 , or $\text{HSi}(\text{OEt})_3$	108
$[\text{Rh}(\text{PPh}_3)_3\text{Cl}]$	Poly(<i>p</i> -diphenylphosphinostyrene)	$\text{CH}_2=\text{C}(\text{Me})\text{COOMe}$, $\text{CH}_2=\text{C}=\text{CHMe}$, $\text{CH}_2=\text{CHCMe}_3$, $\text{CH}_2=\text{CHOEt}$, or $\text{CH}_2=\text{CH}(\text{CH}_2)_4\text{Me}$ with $\text{HSi}(\text{OEt})_3$	8

first use effectively eliminates the third possibility. It perhaps should remain a possibility, although an unlikely one, in the supported palladium(II) catalysis for the addition of Cl_3SiH to butadiene. These polymer-supported catalysts are more active than their homogeneous analogs (suggesting that reaction occurs on the surface), but the palladium is pulled off the surface and left in the liquid as palladium metal so that the catalyst cannot be reused (20).

A distinction between mechanisms i and ii is not easy, and indeed both probably occur. In support of mechanism i, it has been found that in some cases the overall yield following reuse of polymer-supported catalysts is greater than for the corresponding homogeneous catalyst (20). Furthermore, differences between the selectivity of supported and homogeneous catalysts have been noted (20), the selectivity of the supported catalyst being the greater. This latter point is particularly well illustrated by the greater optical yield obtained when a supported catalyst is used in the hydrosilylation of isobutyrophenone as compared to the corresponding homogeneous catalyst (see below) (28). In support of mechanism ii, some authors have observed that part of the metal complex is abstracted out of the support into solution during the reaction (27). The fact that only a proportion of the metal suffers this fate supports the reversibility of the attachment of the metal complex to the polymer.

An investigation of the influence of surface area on the activity of the supported catalysts has shown that the activity increases with increase in surface area, but the selectivity is virtually independent of surface area (27). This result is consistent with both mechanisms i and ii. Thus, in mechanism i the reaction takes place in the pores of the catalyst, which are sufficiently large not to impose steric demands on the reactants, so that the activity of the catalyst is dependent on the rates of diffusion of the reactants to the active site. In terms of mechanism ii, in which the supported complex acts only as a precursor of a soluble catalytically active species, the activity of the catalyst will depend on the ease with which this species is abstracted from the polymer support; clearly, this will increase with increasing surface area.

The specificity with respect to the silane of the rhodium- and platinum-based catalysts are complementary since the order of activity of the rhodium catalysts is $\text{HSi}(\text{OEt})_3 > \text{HSiEt}_3 > \text{HSiCl}_3$, whereas for



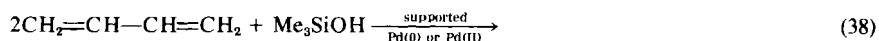
(I)

the platinum catalysts it is $\text{HSiCl}_3 > \text{HSi(OEt)}_3 > \text{HSiEt}_3$ (20). These specificities are the same as found for the corresponding homogeneous catalysts.

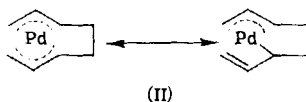
A very important example of substrate specificity was observed in the asymmetric hydrosilylation of ketones using a catalyst based on polystyrene containing the optically active diphosphine (I). Thus, whereas the optical yields obtained on treating acetophenone with dihydrosilanes were very similar to those obtained with the corresponding homogeneous catalyst, with isobutyrophenone it was found that the supported catalyst gave a significantly higher optical yield than the homogeneous catalyst (28). This finding strongly suggests that the support plays a specific role in the catalysis, which would, of course, be analogous to the role of the groups surrounding the active site in many metalloenzymes (53). Clearly, such specificity imparted to the catalyst by the substrate suggests that supported catalysts may become a very important class of highly specific catalysts in the future. Although it is not certain what specific role the support has in the catalysis, it is suggested that some of the phenyl groups may help to protect the catalytic rhodium species by occupying or blocking vacant sites around the rhodium and, thus, preserve a coordinatively unsaturated species.

The yields obtained with the supported catalysts are usually high but less than with the corresponding homogeneous catalysts. However, several supported catalysts that have no homogeneous equivalent have been prepared (23) (in which cases the supported catalysts could be said to be infinitely better). For many of the catalysts, the yield on the second time of use is slightly greater than on the first and thereafter alters very little.

An interesting hydrosilylation reaction catalyzed by supported palladium complexes occurs between trimethylsilanol and butadiene:



The hydrosilylation is accompanied by butadiene dimerization. Although the catalysts were effective, it was found that during the course of the reaction the metal was pulled off the support and, thus, the major advantage of the supported catalyst, namely ease of separation by filtration at the end of the reaction, was lost (22). It was surmized that this occurred because, during the course of the reaction, an intermediate, e.g.,

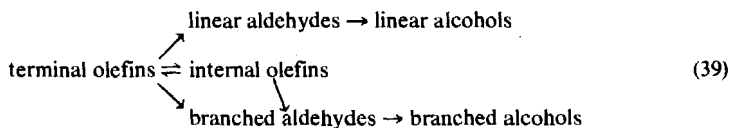


was involved in which the butadiene dimer occupied sufficient coordination sites to displace the palladium from the support. If this explanation is correct, it suggests that polymer-supported catalysts may be of little use whenever the reaction components occupy several coordination sites around the catalyst as in butadiene cyclooligomerization. However, the recent successful use of supported nickel complexes as butadiene cyclooligomerization catalysts suggested that such a pessimistic prediction is unwarranted (93).

C. Hydroformylation

Hydroformylation literally involves the addition of a hydrogen atom to one end of an olefinic double-bond and a formyl group to the other. In practice molecular hydrogen and carbon monoxide are used as the source of these two groups. Cobalt carbonyls and their phosphine derivatives are normally used as catalysts in industrial syntheses (12, 13, 102-104), although a number of rhodium(I) complexes are more effective homogeneous catalysts in that they allow the use of milder conditions in terms of both lower temperatures and lower pressures (29). However, because of their great expense and the difficulty of recovering the catalyst, the rhodium(I) catalysts are rarely used industrially. Since recovery can be facilitated by coordination to a support, there has recently been great interest in supported hydroformylation catalysts, mainly of rhodium(I) but also of the cobalt carbonyl type (Table IV).

The overall reaction of olefins, hydrogen, and carbon monoxide can be complex since not only are both linear and branched aldehydes (and hence alcohols) formed, but the same catalysts promote olefin isomerization. The products formed may be summarized as follows:

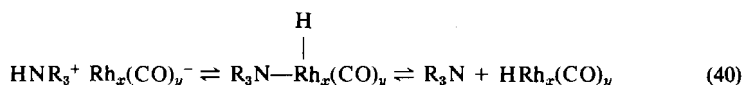


Clearly, then, a given olefin can give rise to a considerable range of products, and one of the features of interest will be to determine how specific is a given catalyst at promoting the formation of a given product. In homogeneous catalyses, it has generally been found that substitution of one or two carbon monoxide ligands by tertiary phosphines leads to significantly greater ratios of linear-to-branched aldehydes and alcohols (31, 51, 62, 102-104, 113); with polymer-supported cobalt carbonyl catalysts, where the polymer has phosphine groups that

have displaced carbon monoxide from coordination to cobalt, the ratio of linear-to-branched products is generally of the order of 2:1 (30), which is similar to the homogeneous phosphine-substituted cobalt carbonyls. Homogeneous rhodium(I) complexes show a similar dependence on tertiary phosphine content, that is, replacement of a carbon monoxide in $[\text{Rh}(\text{acac})(\text{CO})_2]$ by a tertiary phosphine increases the ratio of normal-to-branched aldehydes. Again the polymer-bound catalysts closely resemble their homogeneous counterparts (4).

Both the rhodium and the cobalt complexes catalyze olefin isomerization as well as olefin hydroformylation. In the case of the rhodium(I) catalysts, the amount of isomerization decreases as the ligands are altered in the order $\text{CO} > \text{NR}_3 > \text{S} > \text{PR}_3$. When homogeneous and supported amine-rhodium complexes were compared, it was found that they both gave similar amounts of isomerization, whereas with the tertiary phosphine complexes the supported catalysts gave rather less olefin isomerization than their homogeneous counterparts (44, 45).

The formation of alcohols as an end product is promoted by using more vigorous conditions (both temperature and pressure) for both the cobalt and rhodium catalysts. In the case of cobalt carbonyls, the presence of tertiary phosphine ligands also promotes alcohol formation as well as olefin hydrogenation to the paraffin (102). For rhodium(I) complexes, both homogeneous and polymer-supported, the presence of amine ligands promotes the formation of alcohols; for a given amine, there is an optimum concentration, the optimum decreasing as the basicity of the amine increases (57). This is consistent with the notion that the role of the amine is to promote the formation of a hydrido complex,



which is thought to be the active intermediate in hydrogenation of aldehydes over cobalt and rhodium complex catalysts (50, 71).

Relatively few hydroformylations using supported cobalt complexes have been reported. Moffat (78, 79) showed that poly-2-vinylpyridine reversibly reacted with both $\text{Co}_2(\text{CO})_8$ and $\text{HCo}(\text{CO})_4$, the cobalt carbonyl being displaced by excess carbon monoxide. This enabled the polymer to pick up the cobalt carbonyl at the end of the reaction and, thus, allowed it to be separated from the products by filtration. The polymer acted as a "catalyst reservoir" by rapidly releasing the cobalt carbonyl into solution in the presence of further carbon monoxide, so that the actual catalysis was a homogeneous process. More recently, cobalt carbonyl has been irreversibly bound to a polystyrene resin

TABLE IV
HYDROFORMYLATIONS CATALYZED BY SUPPORTED METAL COMPLEXES

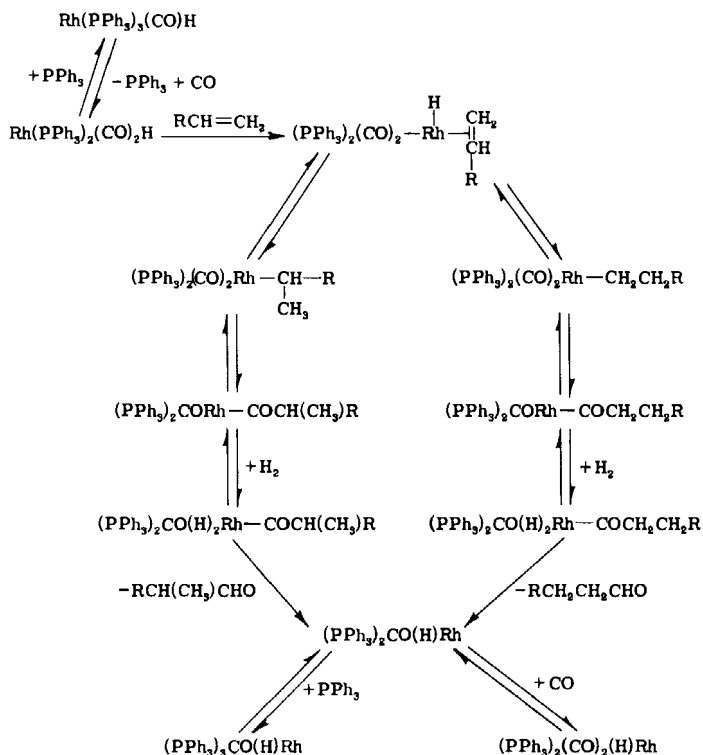
Metal complex	Polymer	Substrate	References
$[\text{Co}_2(\text{CO})_8]$	Poly-2-vinylpyridine and 2-vinylpyridine-divinylbenzene-styrene copolymers	2-Hexene	78, 79
RhCl_3 followed by C_2H_4	Phosphinated 20% cross-linked polystyrene	1-Heptene	21
$[\text{Rh}\{\text{P}(\text{OPh})_3\}_3\text{Cl}]$	Carbon	1-Hexene	11
$[\text{Rh}(\text{CO})_2\text{Cl}]_2$	Cross-linked polystyrene substituted with $-\text{PPh}_2$; $-\text{P}^i\text{Bu}_2$; $-\text{SH}$; $-\text{CH}_2\text{NMe}_2$ or $-\text{P}(\text{OMe})_2$	1-Hexene	45
$[\text{Co}_2(\text{CO})_8]$ $[\text{Rh}(\text{PPh}_3)_2(\text{CO})\text{Cl}]$	Phosphinated chloromethylated cross-linked polystyrene	1-Pentene 2-Pentene	30
$[\text{Rh}(\text{acac})(\text{CO})_2]$	Phosphinated Amberlite XAD-2, phosphinated PVC	1-Hexene	4, 14

[Rh{(EtO) ₃ SiCH ₂ CH ₂ PPh ₂ } ₃ (CO)H]	Silica	1-Hexene	4, 14
[Rh(PPh ₃) ₃ (CO)H]	Phosphinated cross-linked polystyrene	1-Pentene	91
[Rh(PPh ₃) ₂ (CO)Cl]		2-Pentene	
[Rh(PPh ₃) ₂ (CO)Cl]	Silica	Propene	99
Rhodium(I) complexes	Not specified	1-Hexene	44
[RhCl(CO) ₂], [Rh(1,5-COD)Cl] ₂ , [Co(acac) ₃]	Phosphinated silica	Propene	87
RhCl ₃ ·3H ₂ O	Poly-4-vinylpyridine; cross-linked polystyrene substituted with Me ₂ N-, Me ₂ NCH ₂ -, Me ₂ NCH ₂ CH ₂ -	1-Hexene 2-Hexene Cyclohexene	57
[Rh(PPh ₃) ₃ (CO)H]	Phosphinated cross-linked polystyrene	1-Pentene	93
[Rh(PPh ₃) ₂ (CO)Cl] [Rh(AsPh ₃) ₂ (CO)Cl] [Co ₂ (PBu ₃) ₂ (CO) ₆]	Silica gel, alumina, activated carbon, diatomaceous earth	Propene	100

containing $-\text{CH}_2\text{PPh}_2$ groups to give a catalyst that behaves very similarly to its homogeneous counterpart $[\text{Co}_2(\text{CO})_8(\text{PR}_3)_2]$, both in terms of linear-to-branched aldehyde yields and in its promotion of alcohol formation at the relative modest temperature of about 150°C (30).

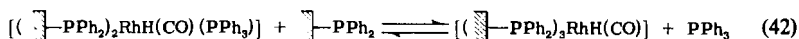
As already mentioned, supported rhodium(I) complexes have virtually the same selectivities as their homogeneous counterparts. In addition, their activities are also very similar to their homogeneous counterparts, except at low temperatures (i.e., close to room temperature) (45, 91, 93); the latter suggests that their activity may under such circumstances be limited by diffusion to and from the catalytic site.

Wilkinson showed that in the homogeneously catalyzed hydroformylation, which follows the mechanism depicted in reaction (41), the first



stage involves replacement of a molecule of triphenylphosphine from the coordination site around rhodium by gaseous carbon monoxide. Clearly, in a supported catalyst, if the phosphine group lost in this stage were that binding the complex to the support, then leaching of the rhodium

from the support would be observed. Experiments to test this have shown that the rhodium content of supported catalysts, far from decreasing on use, actually increases (91)! The increase in rhodium content could be due to chelate formation since this releases bound triphenylphosphine:



The failure to observe any leaching could either indicate that the initial dissociation of the supported phosphine–rhodium(I) bond does not occur or that having been displaced from one site within the support the rhodium subsequently binds to another site. This latter possibility would not lead to any significant leaching in experiments where the catalyst was shaken with the reactants, although, if the reactants were passed through a bed or column of catalyst, leaching should then be observable.

If a large excess of phosphine were present, then the mechanism given in reaction (41) would predict a decrease in catalytic activity. In agreement with this, the activity of supported catalysts does decrease as the ratio of ---PPh_2 to Rh increases (91).

Rony (99, 100) has investigated the activity of hydroformylation catalysts wherein the complex is merely sorbed onto an inert support of silica, alumina, activated charcoal, or diatomaceous earth. Such catalysts can be used to catalyze gas-phase reactions either in the presence or absence of a solubilizing liquid phase, but they are more active when a solubilizing liquid phase is present, probably because this promotes a higher degree of molecular dispersion. Too much liquid phase leads to a decrease in activity, probably because this blocks the pores in the catalyst preventing the reactants, which are in the gas phase, from reaching the catalyst except by a long diffusion through the liquid phase.

D. Carbonylation

Only one group have reported studying a carbonylation reaction catalyzed by a supported catalyst, and this concerns the carbonylation of allyl chloride to yield $\text{CH}_2=\text{CHCH}_2\text{COCl}$ in the presence of $[\text{Pd}(\text{NH}_3)_4]^{2+}$ together with either a monomeric (homogeneous) or polymeric (supported) counterion (43, 44). At low concentrations the two catalysts had the same activities, but, as the catalyst concentration was increased, the homogeneous catalyst became steadily less active due to its aggregation to form a catalytically inactive and insoluble polymeric species. This aggregation is physically prevented in a supported catalyst,

E. Conversion of Acyl Chloride to Ketone

The resulting "fixed-bed" method has advantages in convenience over the homogeneous catalyst although the conditions for the former have not yet been optimized.

F. Dimerization, Oligomerization, and Cyclooligomerization

Some preliminary work on the oligomerization of acetylenes, particularly ethylpropiolate and phenylacetylene, using supported nickel(0) catalysts has been reported (4, 15, 30). The initial products appear to be benzene derivatives (4, 30), although one group (30) reports that reuse of the catalyst yielded some cyclooctatetraene derivatives on the second

TABLE V
DIMERIZATION, OLIGOMERIZATION, AND CYCLOOLIGOMERIZATION CATALYZED BY SUPPORTED METAL COMPLEXES

Metal complex	Polymer	Substrate	References
a. Dimerization of olefins: [Ni(PPh ₃) ₄]	Halogenated cross-linked polystyrene	Ethylene	58
b. Oligomerization of acetylenes: [Ni(PPh ₃) ₂ (CO) ₂]	Phosphinated cross-linked polystyrene	Ethylpropiolate	30
NiCl ₂ followed by treatment of polymer complex with NaBH ₄	Phosphinated PVC	Phenylacetylene	4
NiCl ₂	Phosphinated cross-linked polystyrene	Phenylacetylene, ethyl propiolate	15
c. Cyclooligomerization of butadiene: [Ni(COD) ₂], supported catalyst activated by treatment with AlEt ₂ (OEt)	Phosphinated cross-linked polystyrene	Butadiene	3, 5
[Ni(PPh ₃) ₂ (CO) ₂]	Phosphinated cross-linked polystyrene	Butadiene	93

and subsequent runs. However, the reasons for this change are unclear, partly because the precise nature of the nickel species on the catalyst has not been determined.

Although Wilke has shown that $[\text{Ni}(\text{COD})_2]$ in the presence of tertiary phosphines makes a good catalyst for the conversion of butadiene to C_8 cyclooligomers (114), a supported catalyst of $[\text{Ni}(\text{COD})_2]$ on phosphinated cross-linked polystyrene had very low activity for this reaction. However, when the catalyst was treated with diethylaluminum ethoxide, the activity increased dramatically (3). The diethylaluminum ethoxide is thought to break up any chelated phosphine species by complexing with the dissociated phosphine groups. This is consistent with the observation that $[(\text{---PPh}_2)_2\text{Ni}(\text{COD})]$ was also ineffective as a catalyst, probably due to having two chelated phosphine groups present (4) and thus, inhibiting the loss of one of them to form the active intermediate $\text{R}_3\text{PNi}(\text{C}_8\text{H}_{12})$ (114).

By contrast, the bisphosphine-anchored catalyst described as $[(\text{---PPh}_2)_2\text{Ni}(\text{CO})_2]$ was found to be very similar in activity—both molar turnover rate and product distribution—to its homogeneous counterpart $[(\text{PPh}_3)_2\text{Ni}(\text{CO})_2]$ in the cyclooligomerization of butadiene (93). Indeed, the only important difference between the supported and the homogeneous catalyst was in the rate; the supported catalyst required a temperature of 115°C to achieve the same rate as that of the homogeneous catalyst at 90°C .

G. Polymerization

A number of metal ions coordinated to polymeric ligands have been used to initiate polymerization of vinylic monomers (Table VI). However, the literature reports are scant, and it is difficult to compare the polymeric catalysts with their homogeneous analogs. At first sight, one of the main advantages of the supported catalyst, namely its ease of separation after reaction, would seem to be lost because the polymeric product itself will also be insoluble if a high molecular weight is achieved. Accordingly, one must look for advantages in the ease of polymerization, but the data are inadequate for this purpose.

H. Isomerization

Relatively little has been reported on the "intentional" isomerization of olefins over supported catalysts, although, as mentioned in Section

TABLE VI
POLYMERIZATION USING SUPPORTED METAL CATALYSTS

Metal salt	Polymer	Substrate	References
Mn(II), Fe(II), Co(II), Ni(II) Cu(II), Zn(II), Cd(II)	Copolymers of methylmethacrylate and <i>N</i> -methyl- <i>N</i> -(4'-salicylideneaniline) acrylamide	Styrene	65
CuCl ₂	Polyvinylpyridine quaternized with benzyl chloride	2,6- Dimethylphenol	112
	Polyvinylpyridine	2,6- Dimethylphenol	111
	Polyvinyl alcohol	Methylmethacrylate	60
	Polyvinylamine	Vinyl monomers	54, 59
Mn(III), Cu(II)	Amberlite 1R4B	Butadiene	6
Ni(II), Co(II), Mn(II)	Poly- β -keto esters	Styrene	26
[Zr(π -C ₃ H ₅) ₄], [Nb(π -C ₃ H ₅) ₄], [Cr(π -C ₄ H ₉) ₃]	Alumina, silica	Ethylene	19

III,C, isomerization often accompanies hydroformylation. It has, however, been found that $[(\text{PhCN})_2\text{PdCl}_2]$ absorbed onto silica gel is 100 times more active for the isomerization of α -olefins, such as 1-heptene, than is the same complex alone (116). This implies some specific role for the silica gel. Attempts to use rhodium(III) chloride absorbed onto silica gel, alumina, activated charcoal, and diatomaceous earth as α -olefin isomerization catalysts showed that all these catalysts were unstable even at room temperature (100).

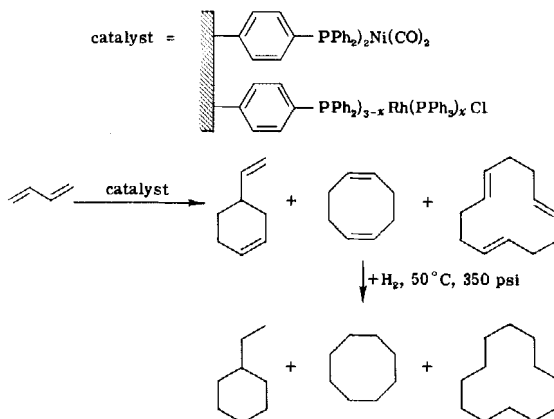
I. Oxidative Hydrolysis and Acetylation

The oxidative hydrolysis and acetylation of olefins in the presence of palladium(II) salts are well-established as commercial routes to acetaldehyde and vinylacetate (46). Both processes have been investigated using supported catalysts. The oxidative hydrolysis has been briefly studied using palladium(II) chloride supported on a cross-linked polystyrene resin containing cyano groups (64). Oxidative acetylation was effected using palladium(II) chloride supported on phosphinated silica (5).

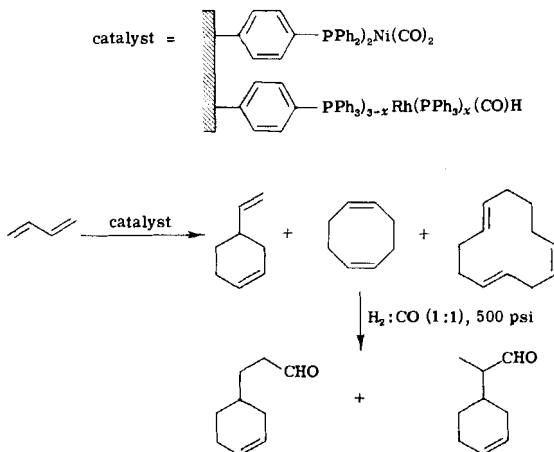
J. Sequential Reactions

Although attempts to bind two catalysts to one support have been reported in enzyme immobilization studies (80), there has only been one report of a similar study using supported transition metal complex

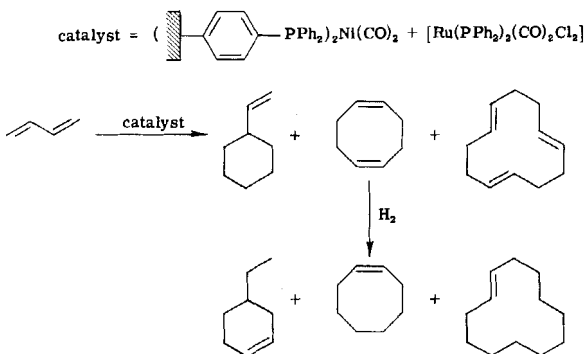
Scheme 1
Sequential cyclooligomerization and hydrogenation:



Sequential cyclooligomerization and hydroformylation:



Sequential cyclooligomerization and selective hydrogenation to monoenes:



SCHEME 1

catalysts in which two different complexes were bound to the same support, and the product of reaction of the first catalyst was used as the substrate for the second (92). Clearly, such an approach is more difficult than using two separated catalysts in two separate reaction vessels since a number of complications may arise: (a) the catalysts may not act individually but may interfere with each other; (b) it is possible that either catalyst may be destroyed by products formed in the presence of the other; and (c) additional side-products may be formed due to one catalyst promoting extra reactions of the product of the other catalyst.

In spite of these difficulties, the sequential reactions shown in Scheme 1 have been attempted (92). In the case of sequential cyclooligomerization and hydroformylation, it was found that the two catalytic species

did not interfere at all. With sequential cyclooligomerization and hydroformylation, the yield of aldehyde dropped from 100 to about 85% in the presence of both catalysts simultaneously. This result was ascribed to the presence of small amounts of triphenylphosphine released into solution from the nickel(0) catalyst, thus impeding the hydroformylation step. In the case of sequential cyclooligomerization followed by selective hydrogenation to monoene, it was found impossible to have both metal complexes present in the same polymer since at the temperatures at which the ruthenium catalyst was used, the nickel catalyst was destroyed. However, the reaction could be effected by using a supported nickel(0) complex together with the homogeneous ruthenium(II) catalyst $[\text{Ru}(\text{PPh}_3)_2(\text{CO})_2\text{Cl}_2]$, because the homogeneous ruthenium(II) catalyst allowed the reaction temperature to be kept below the decomposition temperature of the nickel(0) catalyst. In conclusion, these studies have shown that, although sequential reactions may be carried out using two different metal complexes on a single support, many additional complications will have to be overcome before the possibility becomes a reality.

IV

CONCLUSIONS

It is very clear that the field of supported transition metal complex catalysts is a rapidly expanding field. Indeed, only their application to hydrogenation, hydrosilylation, and hydroformylation reactions have received more than a preliminary skirmish. Already a number of points are becoming clear.

1. Supported catalysts live up to their original purpose of being easily separated at the end of the reaction. Indeed, one of their remarkable features, in view of the mechanisms of the reaction of some of their homogeneous counterparts, is their reluctance to allow the metal complex to be leached out.

2. It was hoped that the presence of the support might in some cases increase the specificity of the catalyst and this has clearly been observed in, for example, hydrogenation and hydrosilylation catalysts, where some supports result in considerably greater specificity than is attainable by the homogeneous catalyst alone.

3. Although diffusion to and from the active site results in many supported catalysts being less active than their homogeneous counterparts, there are an encouraging number of supported catalysts showing activities of between 80 and 100% of the corresponding homogeneous

catalysts. This coupled with ease of separation and possible greater specificity is likely to ensure that supported complex catalysts have a future. However, there are a number of examples coming to light where the supported catalysts have much greater activities than their homogeneous counterparts because the support is able to prevent harmful side-reactions, such as dimerization of the active species.

4. Supported catalysts have the advantage over homogeneous catalysts that they can be used in the presence of any solvent. Since most of the reactions of interest are somewhat dependent on solvent, the solvent can be freely optimized without any restraints being imposed by the catalyst.

In conclusion it is fair to say that, although supported transition metal complex catalysts have only recently been investigated, a sufficient number of encouraging results have been obtained already to allow us to predict that they clearly have an important future.

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Structures of Main Group Organometallic Compounds Containing Electron-Deficient Bridge Bonds

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I

INTRODUCTION

The early developments in the chemistry of boron hydrides and aluminum alkyls quickly led to the realization that these species did not conform to the accepted theories of bonding, but required the development of new concepts that could account for the dimeric or polymeric nature of these derivatives. These concepts, were initially provided in a number of papers by Mulliken (88), Longuet-Higgins (70), Pitzer (93), Pitzer and Gutowsky (94), and Rundle (97, 98). Much of this work has been summarized recently in books by Wade (118), by Lipscomb (69),

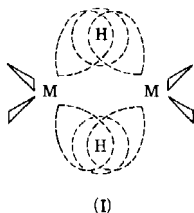
and by Matteson (79), whereas both the chemistry and the bonding of all of the compounds concerned have been dealt with by Coates (27). In addition, several comprehensive reviews and books, which deal with specific derivatives of interest including lithium (20, 21, 80, 120), beryllium (29, 42, 121), magnesium (121), boron (47, 69, 111), and aluminum (62, 82) have appeared.

The purpose of this review is to summarize the recent information available on the structures of derivatives of the main group elements that contain electron-deficient bridge bonds and to focus attention on the relationships between the structures and the bonding in these molecules.

II

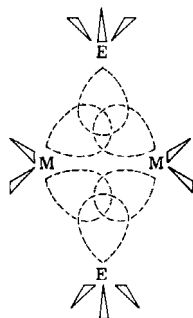
GENERAL DISCUSSION OF BONDING

In order to develop a understanding of the factors that influence the structures of the main group derivatives containing electron-deficient bonds, we must first consider a simplified model for the bonding in these molecules. The bonding in a hydride-bridged system can be visualized in terms of the general diagram (I).



The two metal atoms make use of hybrid orbitals as indicated, and each of these overlaps a hydrogen orbital that is centered midway between the metals but substantially above the metal-metal axis. For a dimeric species, such as diborane, this is repeated with a second set of orbitals and hydrogen atom symmetrically placed on the opposite side of the metal-metal axis. Examination of this model shows that each of the terminal bonds is a "normal" 2-electron-2-center bond. Only the bonds between the metal centers are nonconventional. An extensive review of these systems has been given by Lipscomb (69).

A similar diagram (II) may be drawn for species that make use of carbon or silicon as the bridging atom. In these systems the orbital used for bridge formation may be described in terms of a hybrid orbital from the bridging atom which becomes five- (or six)-coordinate.



(II)

In general, the electron-deficient bonds to be dealt with in this review can be described in the manner given, i.e., by the interaction of the orbital on 3 or more atoms that give rise to a corresponding set of molecular orbitals. Further, the set of molecular orbitals will not be completely filled by the number of available electrons and, thus, leads to the common term, electron-deficient bonding. A second feature, which led to some concern by many chemists, is the common occurrence of two-coordinate hydrogen and five- or six-coordinate carbon. When the bonding is described in terms of molecular orbitals, these higher coordination numbers can readily be understood.

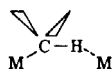
A number of papers have appeared recently in which semiempirical quantum mechanical methods, such as the complete neglect of differential overlap (CNDO), incomplete neglect of differential overlap (INDO), or Hückel methods, have been applied to electron-deficient systems in an attempt to calculate their properties (31, 49, 64, 75, 77, 78, 89, 90, 92). Although the quantitative results of these calculations must be treated with great care, they do provide an indication of some of the parameters that determine formation and stability of electron-deficient bonded systems.

These calculations indicate that, for both the aluminum derivatives and for those formed by the Group II metals, one must consider metal-metal bonding interactions particularly through the use of d orbitals, but also take into account repulsion between these centers. A parameter related to these interactions is the metal-metal distance which on comparison with the sum of the metal covalent radii gives an indication of the relative magnitudes of these terms. Also, we must consider the metal-to-bridging atom distance, which must be related to the stability of the bond and should be compared with normal 2-electron bond distances between these same elements. Further, we should consider the electro-

negativity of both the metal centers involved and of the bridging atom, since charge distribution plays a role in the manner in which these species bond and also react. Some of the parameters of importance are collected in Table I.

In addition, one must consider the possibility of interaction between adjacent groups. This is of particular importance when dealing with the beryllium derivatives in which the metal nucleus is very small and may also be of significance in other systems such as the lithium aggregates. Unfortunately, little quantitative information has appeared with regard to this feature other than statements of distance observed in a few systems.

On several occasions, a different model has been proposed to account for the bridge bonding in metal alkyls. In this model, it has been suggested that the bridge involved 2 atoms with an M—C—H—M interaction:



(III)

As indicated in Section III,A, this does not appear to occur for aluminum derivatives but has recently been revived in discussions

TABLE I
RADII AND ELECTRONEGATIVITY VALUES FOR ATOMS
ENTERING INTO ELECTRON-DEFICIENT BONDING^a

Element	Radii (Å)		Electroneg.
	Atomic	Covalent	
Li	1.5	1.34	0.97
Be	1.12	0.90	1.47
Mg	1.60	1.30	1.14
Zn	1.38	1.31	1.66
Hg	1.57	1.49	1.44
Al	1.43	1.18	1.47
Ga	(1.4)	1.26	1.82
In	1.66	1.44	1.49
Ti	1.45	1.36	1.32
H	—	0.37	2.20
C	0.914	0.77	2.50
Si	1.32	1.11	1.74
Ge	1.37	1.22	2.02

^a Selected values from A. J. Gordon and R. A. Ford, "The Chemists' Companion," pp. 82-87. Wiley (Interscience), New York, 1972.

dealing with lithium alkyls and lithium alkyl metalates (Sections VI and VII).

In this review, emphasis will be placed first on definitive proof of structure for compounds of main group organometallic compounds that contain the electron-deficient or multicentered bonds described. Evidence for the occurrence of these systems in both liquid and gaseous states also will be given. Finally, this structural information will be used to elucidate the bonding in the molecules.

Main group metals that have been shown to form electron-deficient bridged molecules are those having both low electronegativity and small size. These elements are lithium, beryllium, boron, magnesium, aluminum, gallium, and indium. The other more electropositive elements, such as sodium or calcium, appear to form species better described as ionic compounds, whereas the less electropositive derivatives, such as zinc, cadmium, mercury, and thallium, as well as indium and gallium, all form normal covalently bonded organometallic compounds, except in special cases.

The structures and bonding of many boron hydrides have been discussed in an excellent review (69), and more recently the carboranes have been reviewed in detail (47); therefore, neither of these topics will be included in the present work.

In order to accomplish the goals of this reviewer in a logical and systematic manner, the first systems to be described will be those of aluminum derivatives that appear to be the most readily discussed in terms of their structures and bonding, followed by the Group II derivatives of beryllium and magnesium, and, finally, by a discussion of the lithium derivatives and of the mixed-metal species, which clearly represent the most difficult systems to describe properly.

III

ALUMINUM DERIVATIVES

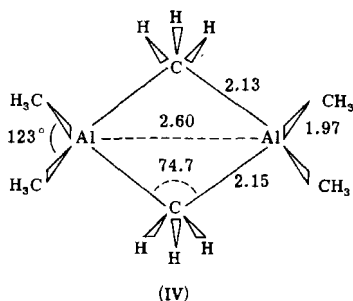
A. Symmetrical Carbon-Bridged Derivatives

The structures of substantial numbers of simple organoaluminum species have been reported during the past few years. The initial structure determined was that of trimethylaluminum (IV) (68). Subsequently, the structure has been redetermined in the solid state (116) and attempts have even been made to determine the location of the hydrogen atoms to provide details concerning the bonding present within this molecule (54).

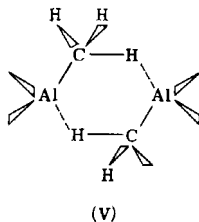
TABLE II
BOND DISTANCES AND ANGLES FOUND IN CARBON-BRIDGED ORGANOALUMINUM COMPOUNDS

Compound	Distances (Å)			Angles (°)			Ref.
	Al—C _b	Al—C _t	Al—Al	Al—C—Al	C—Al—C (internal)	C—Al—C (external)	
Al ₂ Me ₆	2.13 2.15	1.96 1.98	2.60	74.7	105.3	123.1	116
Al ₂ ∇ ₆	2.062 2.098	1.90 1.95	2.618	78.2	96.7	115.2	84
Al ₂ Ph ₆	2.184 2.180	1.960	2.618	76.5	103.5	115.4	74
Al ₂ (Ph) ₂ Me ₄	2.129 2.152	1.965 1.968	2.690	77.5	101.3	121.5	75, 76
Al ₂ (CH=CH- <i>t</i> -Bu) ₂ (<i>i</i> -Bu) ₄	2.10 2.12	1.965 1.999	2.684	79	100.9	128.5	2
Al ₂ (C≡CPh) ₂ (Ph) ₄	1.992 2.184	~3.0	91.7	—	—	—	112

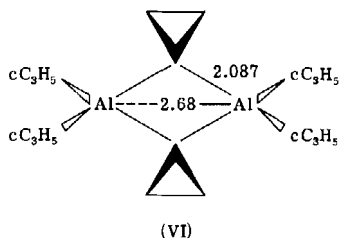
Additional studies have been reported on the electron diffraction of both monomeric and dimeric AlMe_3 in the gas phase, and a variety of other spectroscopic studies have appeared which all support structure IV (7). Several of the most important parameters for this structure and related carbon-bridged species are collected in Table II.



It has been suggested that the bridged dimer is stabilized by metal-hydrogen interactions as indicated in structure V (23). This type of interaction, however, appears to be incorrect for trimethylaluminum, or at least not to result in significant stabilization. The form without hydrogen interaction (IV) has been supported by studies of the nuclear quadrupole resonance (NQR) spectra of the aluminum species (33-35), by low-temperature X-ray studies (54), and from the fact that other systems that cannot possibly have metal-hydrogen interactions due to the orientation of the bridging group form stable bridged dimers (2, 74-76, 84, 112).

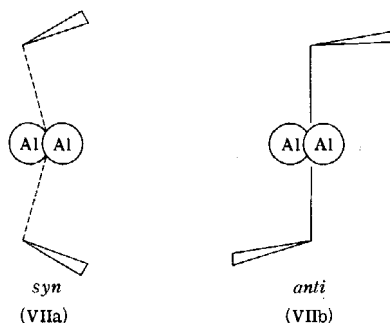


The structures of several other symmetrical organoaluminum compounds, which have important implications with regard to electron-deficient bonding, have been determined from X-ray data. The first of these (VI) shows the structure of tricyclopropylaluminum dimer (84, 99). In this compound, the $\text{Al}-\text{C}-\text{Al}$ bridge is symmetrical and the cyclopropyl rings are oriented so that the p orbital on the bridging carbon atom may interact with the appropriate vacant orbitals on the metal atoms. This interaction appears to increase the stability of the bridge bond as indicated from variable-temperature NMR studies. The

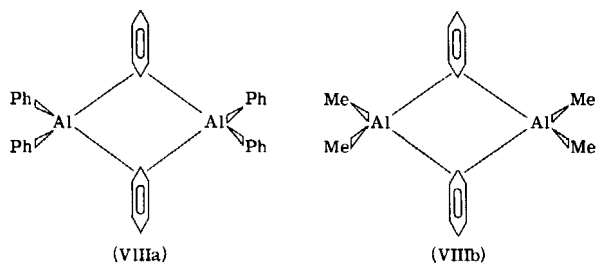


results of these experiments show that bridge terminal interchange occurs only at elevated temperatures, strongly supporting the suggestion that the dissociation of the aluminum derivatives is energetically more difficult (99, 100).

It is suggested that there are two possible conformations for the bridging cyclopropyl groups: the syn form (VIIa) observed in the crystal and the anti form (VIIb) that appears from minimum energy calculations to be more stable in solution (100). These differences and some of the angles seem to result from crystal packing energies in the solid state versus the less constricted form in solution.

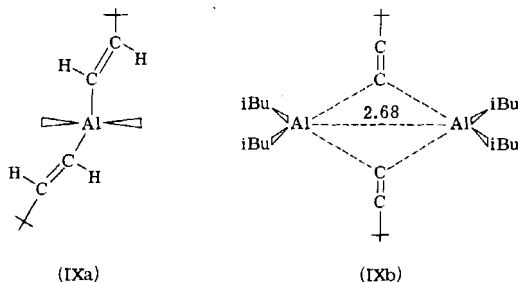


A similar situation prevails in the aromatic derivatives VIIIa and VIIIb (74-76). In these dimeric species, the phenyl groups are oriented perpendicularly to the Al-Al axis so that the π -orbitals on the ring (or the p orbital on the bridging carbon atom) is permitted by symmetry to interact with the vacant nonbonding orbitals on the metal atoms. Again,



spectroscopic studies on solutions of these derivatives imply that the bridging phenyl groups result in a lower total energy for the system than when the bridging sites are occupied by methyl groups. This assumption is supported by the preferential location of the bridging positions.¹

One might anticipate similar results for a vinyl-bridged species with stabilization resulting from interaction of the π -electrons with the vacant nonbonding metal orbitals. Cryoscopic and spectroscopic evidence has been used to show that trivinylgallium, unlike the alkylgallium derivatives, is dimeric in solution (91, 117), thus lending credence to the suggestion (87). Further, this has been demonstrated for several vinylaluminum derivatives, again on the basis of spectroscopic studies (16, 33, 41, 137).

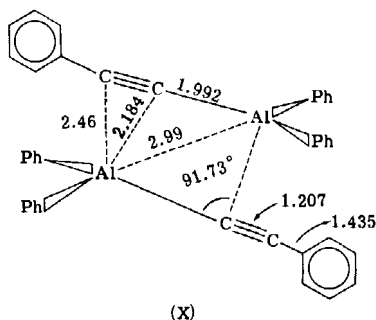


Confirmation of this proposal is now available from the recently completed structure of $(i\text{-Bu})_2\text{Al}(\text{trans-CH=CH-}t\text{-Bu})$ dimer (IX) (2). In this structure the Al—Al and bridging Al—C distances are reasonably normal for these electron-deficient systems and the bridging groups are located equally between the 2 aluminum atoms, with the plane described by the C=C—C fragment perpendicular to the Al—Al axis. One difference between this structure and those of the other systems discussed that may have metal- p orbital interactions is that the bridging groups are in the anti conformation as seen when the molecule is viewed down the Al—Al axis (IXa) with little or no distortion in the Al—C—Al—C four-membered ring in the solid state. This provides further support for the idea that the distortions in the other systems result from crystal packing forces.

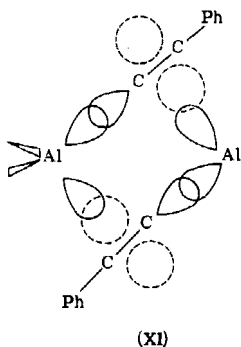
Finally, systems containing ethynyl bridging groups will be considered. These groups have been shown to enter effectively into bridge bond formation and, in fact, appear to form the most stable carbon-

¹ An anomalous finding for the aromatic systems is the unusually low-energy exchange path recently reported for the tolyl aluminum derivatives; it is accounted for by a difference in exchange mechanism and not by a decrease in the stability of the bridge bond (110).

bridged aluminum (39, 59, 83), gallium (58), and indium (58) derivatives known. Initially, it was proposed that the bridging was similar to that found for the vinyl systems, but a recent structure determination has been reported indicating that this is not the correct description (112). In fact, the structure of diphenyl(phenylethynyl)aluminum dimer (X) demonstrates that the bridging groups are placed unsymmetrically between the two metal atoms.



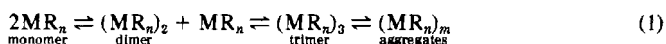
In this compound, the bonding from the bridging group to one aluminum is principally σ in character, whereas that to the second aluminum atom results primarily from overlap of the π -orbitals of the triple bond with the vacant p orbital on the aluminum atom. This is evident from the structural parameters that show a wide Al—C—Al angle and a very long (~ 3.0 Å) Al—Al distance out of the range associated with other bridged derivatives (see structure XI). This difference in bonding between the electron-deficient systems shown for the alkyl, vinyl, and aryl systems and for the phenylethynyl system may account for the unusual stability not only for the phenylethynylaluminum dimer but also for the stability of the gallium and indium species that are dimeric in solution.



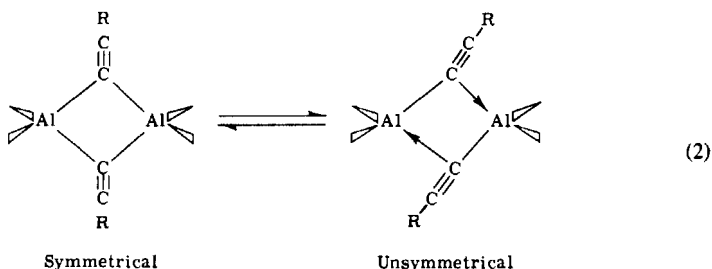
Further support for this difference between the bonding with the

ethynyl groups and other bridging moieties has been suggested on the basis of the structure of $[\text{Be}(\text{C}\equiv\text{CPh})_2\text{NMe}_3]_2$, which shows distortion of the bridge bond from the normal symmetrical arrangement (86) (for further details, see Section V,A). Additional work is called for on compounds that contain unsaturated bridging groups in order to determine what factors alter the stability and conformations of these species.

In dealing with the various types of carbon bridging, it appears that one has a competition among several possible types of bond formation which result in small structural changes or changes in the degree of aggregation. Alterations in the degrees of aggregation may be described as follows:



For the aluminum systems so far described, only the monomer–dimer equilibrium has been observed. For very bulky R groups, the monomer predominates; for small alkyls, cyclopropyl, and phenyl-bridged species, the symmetrical dimer is the stable form. When the phenylethynyl group is present, this equilibrium is complicated further by the additional feature arising from the different possible types of bridge bonds, which may be described in the following manner:



The observed species is again determined by the total energy of the system. In the solid state, the unsymmetrical species is favored for the phenylethynyl derivatives, implying that two symmetrical bridges are less stable for this system than two σ -bonds plus two $\pi \rightarrow$ metal interactions, whereas for the *trans*-(*t*-butylvinyl) derivative, the symmetrical arrangement is favored.

Similar $\pi \rightarrow$ metal interactions have been suggested for the intramolecular interaction of an olefin with aluminum in terminal olefin derivatives of the type $\text{Al}[(\text{CH}_2)_n\text{CH}=\text{CH}_2]_3$, which have been shown to be monomeric in solution even though the corresponding $\text{Al}[(\text{CH}_2)_{n+1}\text{CH}_3]_3$ alkyl derivatives are predominantly dimeric with bridging alkyl groups under similar conditions (37).

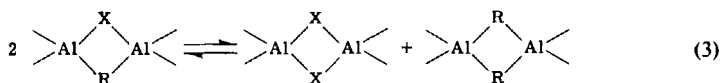
From these facts and the known heats of dimerization of the alumi-

num compounds, one may estimate that the heat of $\pi \rightarrow$ metal interaction for the terminal olefin system is of the order of 4–8 kcal/mole (108). Comparable data are unavailable for the ethynyl derivatives, but it seems likely that the $\pi \rightarrow$ metal interaction must be greater in these systems to account for the stability of the unsymmetrical form and the high degree of stability of the dimer.

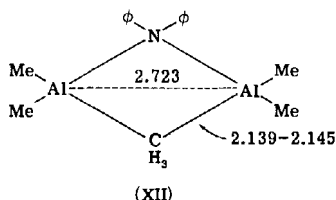
B. Species Containing Dissimilar Bridging Groups

A number of systems have been described in which all available evidence indicates that two types of bridging groups are present. These include compounds such as pentamethylcyclopropyldialuminum (84, 100), other species where both bridging atoms are carbon (58, 110), as well as systems with one carbon bridge and one hydrogen bridge (26), resulting in two electron-deficient bridge bonds of differing stability.

No such compounds have been characterized by structural studies, but both the mixed cyclopropyl–methyl bridged dimer and the phenyl–or tolyl–methyl bridged dimer (57, 110) have been well studied by NMR. A simple analysis of the stability of this type of species suggests an equilibrium among the following dimeric species:



The number of electron-deficient and normal bridge bonds remains constant throughout, but, from the very limited information available (other than by the inference from the fact that few mixed bridged species of this type have been isolated), the mixed bridged species is thermodynamically unstable with respect to the two symmetrical dimers.



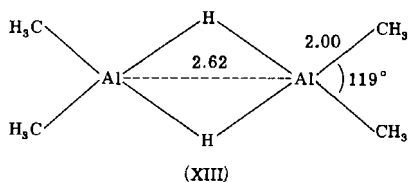
A second class of unsymmetrically bridged systems is represented by pentamethyl(diphenylamino)dialuminum in which the bridging atoms are different, one providing an electron-deficient bridge bond and the other a normal bridge with two electron bonds (11, 40, 43, 51, 57, 59, 61, 71, 72, 110). The only species of the latter type for which structure has been

determined is $\text{Al}_2\text{Me}_5\text{NPh}_2$ (XII), which contains a bridging diphenylamino group and a bridging methyl group (71, 72). Both the Al—Al distance and the Al—C distances are similar to those observed in trimethylaluminum dimer. A number of other compounds of this type have been reported and well characterized by spectroscopic or chemical means, but structural studies have not been carried out. These include $\text{Me}_5\text{Al}_2\text{N}(\text{SiMe}_3)_2$ (130), $\text{Me}_5\text{Al}_2(\text{O}-t\text{-Bu})$ (57), $\text{Me}_5\text{Al}_2(\text{O}-i\text{-Pr})$, $\text{Me}_5\text{Al}_2(\text{N}=\text{CMePh})$ (57), $\text{Me}_5\text{Al}_2\text{Cl}$ (51), and $\text{Me}_5\text{Al}_2\text{OCPh}_2\text{Me}$ (11) among others.

Work dealing both with the structures of these derivatives, especially those containing the more unusual bridging species, such as those containing double or triple bonds, should provide a substantially better description of the bonding associated with electron-deficient systems.

C. Systems Containing Hydride Bridges

Introduction of a hydride bridge leads to mixed bridged species, but a further complication is often involved, namely the formation of trimers or higher aggregates. For several mixed vinyl-hydride systems, it has been suggested on the basis of NMR spectral studies that the species are dimeric with one hydrogen and one vinyl bridge (26). It also has been suggested that trimers exist in these systems (41). When alkyl groups are present, such as in dimethylaluminum hydride (122) or diisobutylaluminum (135) hydride, then trimers are observed in solution and a mixture of dimers and trimers in the gas phase (122). Mass spectral studies confirm this both for dimethyl- and diethylaluminum hydride (24, 114).



The structure for the $(\text{Me}_2\text{AlH})_2$ dimer (XIII) has been determined from gas-phase electron diffraction studies (4, 9). Examination of the data in Table III and those in Table IV, for both the electron-deficient bridged systems and the normal bridged aluminum dimers, show that this compound has a typical electron-deficient bridged structure.

These systems can again be described in terms of Eq. (1) in which the energetically favored species has become the higher aggregate. No

TABLE III
STRUCTURAL PARAMETERS FOR A VARIETY OF BRIDGED ORGANOALUMINUM DERIVATIVES

Compound	Al—Al distance (Å)	Al—X bridge distance (Å)	Al—C terminal distance (Å)	Al—X—Al bridge angle (°)	Al—C terminal angle (°)
$\text{Al}_2(\text{NPh}_2)\text{Me}_5^a$	2.723	2.14 (Al—C) (Al—N)	—	— —	— —
$\text{Al}_2(\text{NMe}_2)_2\text{Me}_4^b$	2.737	1.96 (Al—N)	1.96	96.3	120
$\text{Al}_2(\text{NCMe}_2)_2\text{Me}_4^c$	—	1.946 (Al—N)	1.97	—	114
$\text{Al}_3(\text{n})_3\text{Me}_6^d$	—	1.91–1.95 (Al—N)	1.99	—	116
$[\text{Al}(\text{NMe}_2)\text{Me}_2]_2^e$	2.809	1.95 (Al—N)	1.95	—	118
$[\text{Al}(\text{NMe}_2)\text{Me}_2]_3^e$	3.4	1.95 (Al—N)	1.97	—	131
$(\text{AlFMe}_2)_4^f$	—	1.81 (Al—F)	1.95	—	119
$\text{Al}_2\text{H}_2\text{Me}_4^g$	2.62	—	2.00	—	—

^a Reference 72.

^b H. Hess, A. Hindener, and S. SteinHauser, *Z. Anorg. Allg. Chem.* **337**, 1 (1970).

^c S. K. Seale and J. L. Atwood, *J. Organometal. Chem.* **73**, 27 (1974).

^d Reference 15a.

^e G. M. McLaughlin, G. A. Sim, and J. D. Smith, *J. Chem. Soc., Dalton Trans.* 2197 (1972).

^f Reference 10.

^g Reference 4.

TABLE IV
STRUCTURAL PARAMETERS FOR SELECTED COMPOUNDS CONTAINING NORMAL AL—C
AND AL—N BONDS

Compound	Al—C distance (Å)	Al—N distance (Å)	Al—X distance (Å)
Me ₂ Al·NMe ₃ ^a	1.95	1.97	2.59 (Al—I)
Me ₃ Al·NMe ₃ ^b	1.99	2.099	—
K[Me ₃ Al(N ₃)AlMe ₃] ^c	1.99	2.02	—
K(Me ₃ AlN ₃) ^d	1.99	1.97	—
K(Me ₃ AlCN) ^e	1.97	—	2.05 (Al—CN)
Rb(Me ₄ Al) ^f	2.06	—	—

^a J. L. Atwood and P. A. Milton, *J. Organometal. Chem.* **52**, 275 (1973).

^b G. A. Anderson, F. R. Forgard, and A. Haaland, *Acta Chem. Scand.* **26**, 1947 (1972).

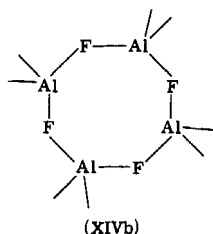
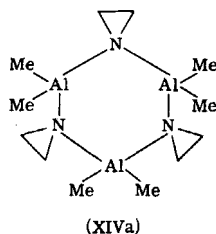
^c J. L. Atwood and W. R. Newberry, III, *J. Organometal. Chem.* **42**, C77 (1972).

^d J. L. Atwood and W. R. Newberry, III, *J. Organometal. Chem.* **87**, 1 (1975).

^e J. L. Atwood and R. E. Cannon, *J. Organometal. Chem.* **47**, 321 (1973).

^f J. L. Atwood and D. C. Hrnčir, *J. Organometal. Chem.* **61**, 43 (1973).

structures of such compounds have appeared in the literature, but structures of both trimers (XIVa) (15a) and tetramers (XIVb) (10) of electron precise compounds have been reported; they are cyclic with normal Al—C terminal bonds as seen on comparison of the data in Tables III and IV. It is probable that similar structures will be observed for the aluminum trimers and higher aggregates containing hydride bridges.



D. Bonding Studies

Limited studies have appeared in which efforts have been made to calculate bonding parameters for hydride and carbon-bridged aluminum dimers (31, 64, 65, 66, 78, 89, 90, 100), making use of several semiempirical methods. Most of the results of these procedures show some agreement in the gross features of the bond, but all suffer due to the approximations made and, thus, do not presently provide a clear understanding of the bridge bond present in these systems. All ap-

proaches indicate some metal-metal interaction, and it has been suggested by several of the authors that this metal-metal interaction provides the stabilization of the dimer over the monomer for these derivatives.

If substantial stabilization results from metal-metal interactions, then the large Al—Al separation (approximately 3.0 Å) observed in the phenylethynyl-bridged aluminum compound is of major importance since it would lead to greatly reduced metal-metal interaction. This would require that the estimate of $\pi \rightarrow$ metal interaction is far too low and would, in fact, have to be of the order of 15 kcal/mole to account for the stability of the dimeric species.

Other features, which one might look at, are the charge density on the carbon and aluminum atoms as calculated by the various methods. Most studies suggest relatively high positive charge on the aluminum with negative charge residing on the bridging atom. The values of the calculated charges vary widely, and, in fact, in one sequence of calculations they are reversed with the negative charge residing on the Al atom and positive charges on the bridging groups (64–66).

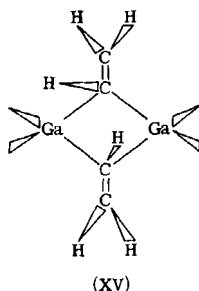
The CNDO calculations on the cyclopropyl-bridged dimer yield reasonable estimates of the barrier to rotation for the bridging cyclopropyl moiety and, at the same time, indicate little change in the Al—Al bond order as a function of rotation of the bridging group. These studies still do not provide a fully satisfactory description of the bond but they do support the qualitative description originally proposed (97, 98).

IV

HEAVIER GROUP III METAL DERIVATIVES

Several studies have appeared showing that dimeric carbon-bridged dimers of gallium and of indium exist in solution; these studies have provided the basis for the bonding model on which p-orbital stabilization was based since these species all contain vinyl or ethynyl bridging groups of unusual stability (91, 117).

The proposed structure for the vinyl gallium species (XV) (117) appears to be on firm ground as a result of the study on the vinylaluminum derivative (2). The ethynyl-bridged gallium and indium (58) species might not have this type of structure, as originally proposed, but may have structures similar to that observed for the phenylethynylaluminum dimer with an unsymmetrical bridging group (112). This should be experimentally tested, and clearly a structure for a vinyl-bridged



dimer should be determined to establish the precise structure of these bridged dimers as well.

Both trimethylgallium and -indium are monomeric in solution (87), and structural studies on the trimethylindium (8) and triphenylindium and -gallium (80) show that these species are not bridged dimeric molecules in the solid state, although there may be some degree of intermolecular interaction. Thus, it appears that bridged molecules of indium or gallium require particularly effective bridging groups such as the vinyl or phenylethynyl moieties.

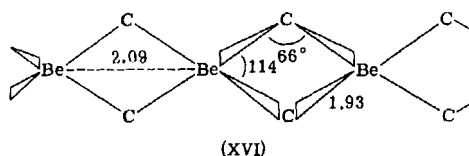
V

GROUP II METAL DERIVATIVES

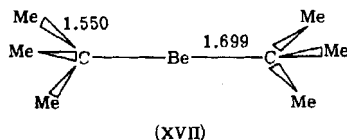
The Group II metals, beryllium, magnesium, calcium, zinc, cadmium, and mercury, will all be considered briefly with regard to their ability to form electron-deficient structures. The electronic structure of these elements provides one less bonding electron than for the Group III elements and, consequently, provides an additional vacant orbital with fewer bonding electrons. This feature may lead to four-coordinate metal atoms in polymeric materials or to three-coordinate metal atoms in dimers. If the additional criteria stated earlier are applied, then mercury and probably cadmium can be ruled out as reasonable choices for formation of electron-deficient bridges due both to their electronegativity and their size. Zinc seems like a reasonable candidate, especially in view of its covalent radius (1.31 Å) and electronegativity (1.66), which are reasonably close to those of several metals that readily form electron-deficient bridged species. Despite this, no electron-deficient species have been confirmed for zinc derivatives by structural studies. Similarly, no definitive evidence for electron-deficient compounds has been reported for calcium or the higher congeners. This latter appears to

result from the low electronegativity and large cation size of these metals. These factors result in formation of essentially ionic species and not covalently bound electron-deficient molecules. Thus, we are left with established cases of electron-deficient bonding only for beryllium and magnesium.

A. Beryllium Derivatives

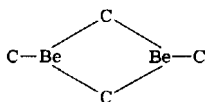


Only a limited number of structural studies have been reported on beryllium compounds. The simple alkyls appear to be polymeric with chain structures as shown in XVI (109). For comparison, the structure of di-*(t*-butyl)beryllium (XVII) is shown as determined from electron diffraction studies (6). In this case, the compound is a linear monomeric species with a Be—C bond length of 1.699 Å. Similarly, dimethylberyllium has a Be—C bond distance of 1.70 Å in the gas phase (5). Comparison of these beryllium structures with the polymer shows that the Be—C distance in the bridge is considerably greater than that in a normal Be—C single bond, a result similar to that observed for the aluminum derivatives.

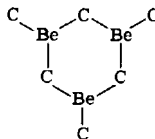


There are several interesting features that result from the small size of the beryllium atom. These include the short metal-metal distances observed in the polymeric materials and the sharp Be—C—Be angle of 66° observed in the BeMe₂ chain structure. The fact that di-*(t*-butyl)beryllium is monomeric in solution is also a result of this since the short Be—C and Be—Be bond distances lead to steric interactions between the *t*-butyl groups preventing dimer formation. The general problems concerning the degree of aggregation for beryllium alkyls have been discussed by Coates and Morgan (29). They considered various factors in aggregate formation including the formation of the dimer (XVIII) and cyclic trimer (XIX) which have three-coordinate beryllium atoms. This reduces the steric interference arising from interaction of

the substituent groups, but the dimer energy is reduced by "angle strain" and by possible across ring interactions, whereas the trimer is less favorable on the basis of the entropy loss associated with a reduction of the translational degrees of freedom associated with more particles.

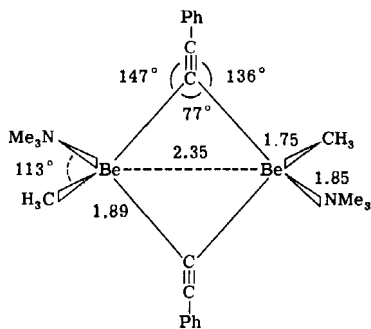


(XVIII)



(XIX)

A further point of interest is that in both the dimeric and trimeric species shown, the beryllium atom still has a vacant orbital available which may be used in adduct formation without disruption of the electron-deficient bond. This type of behavior leads to the formation of dimers with four-coordinate beryllium atoms, e.g., structure XX (86). This structure has been determined in the solid state and shows that the phenylethynyl-bridging group is tipped to the side, but to a much smaller extent than observed in the aluminum derivative (112). One cannot be certain whether the distortion in this case is associated with a $\pi \rightarrow$ metal interaction or is simply a result of steric crowding, crystal packing, or the formation of the coordination complexes. Certainly some differences must have occurred since both the Be—Be distance and Be—C—Be angle are substantially increased in this compound relative to those observed in the polymer chain.



(XX)

The structural data for these systems are collected in Table V along with data for several other beryllium derivatives including the simple hydrides that also form electron-deficient bridged systems of high stability.

TABLE V
STRUCTURAL PARAMETERS FOR BERYLLIUM DERIVATIVES

Compound	Distances (Å)		Angles (°)		Ref.
	Be—Be	Be—X	C—Be—C	Be—C—Be	
$[(\text{BeMe}_2)_n]$	2.09 ± 0.01	1.93 ± 0.02 (bridge)	114 ± 1	66 ± 1	109
$(\text{MeBeC}\equiv\text{CMe}\cdot\text{NMe}_3)_2$	2.35	1.89 (bridge)	103	77	86
BeMe_2 (monomer)	—	1.698	—	—	5
$\text{Be}(t\text{-Bu})_2$ (monomer)	—	1.699	—	—	6
$[\text{Be}(\text{NMe}_2)_2]_3$ (linear)	2.30	1.65 (Be—N)	—	—	13
$\text{Be}[\text{N}(\text{SiMe}_3)_2]$ (gas phase)	—	1.562 (Be—N)	—	—	^a
MeBeCp (gas)	—	1.706 (Be—C)	—	—	^b
		1.923 (Be—C _s ring)			
$\text{Me}_2\text{Be}\cdot 2\text{-quinuclidine}$	—	1.85 (Be—C)	—	—	^c

^a A. H. Clark and A. Haaland, *Acta Chem. Scand.* **24**, 3024 (1970).

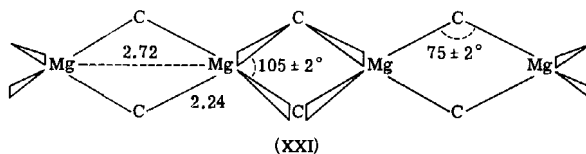
^b D. A. Drew and A. Haaland, *Acta Chem. Scand.* **26**, 3079 (1972).

^c C. D. Whit and J. L. Atwood, *J. Organometal. Chem.* **32**, 17 (1971).

Limited theoretical studies (31, 89) on the electron-deficient beryllium derivatives have been interpreted to imply that extensive Be—Be bonding occurs. If such bonding does occur, the increased bond length observed in the phenylethynyl(methyl)beryllium trimethylamine adduct takes on additional significance since the Be—Be distance in this derivative is increased by almost 0.3 Å over that observed in dimethyl- and diethylberyllium. Moreover, if cyclic trimers are formed, then increased metal-metal distances would be likely, thus reducing the probability of stabilization of the bridged system by Be—Be bonding. Additional studies will be required both on structures and of spectroscopic properties of the species to answer these questions.

B. Magnesium Derivatives

The only magnesium compounds for which structures have been reported that contain electron-deficient bonds are those of dimethyl (123)- and diethylmagnesium (124). The structure common to these two derivatives is XXI, and the data for these compounds along with those from a variety of other organomagnesium derivatives are collected in Table VI for comparison. Clearly, insufficient data are available to draw any specific conclusions concerning the electron-deficient derivatives, but no unexpected deviations appear in the compounds studied.



The Mg—C distance in the bridge are somewhat longer than the Mg—C single-bond distances observed in the Grignard-type reagents, but comparisons cannot be made with a simple dialkyl since none of the structures have been reported. The Mg—Mg distance is about 2.70 Å, which is relatively short and could permit metal-metal interaction for stabilization of the polymeric materials, as suggested for the beryllium derivatives, but neither sufficient experimental data nor theoretical calculations (90) are available to confirm or refute this possibility.

VI

STRUCTURE OF ORGANOLITHIUM DERIVATIVES

An examination of the size (1.34 Å), electronegativity (0.97), and electronic structure of lithium show that this element differs substan-

TABLE VI
STRUCTURAL PARAMETERS FOR MAGNESIUM DERIVATIVES

Compounds	Distances (Å)		Angles (°)	
	Mg—Mg	Mg—C	C—Mg—C	Mg—C—Mg
$[\text{Mg}(\text{Me}_2)]_n$ ^a	2.72 ± 0.02	2.244 ± .03	105 ± 2	75 ± 2
$[\text{MgEt}_2]_n$ ^b	2.67 ± 0.01	2.26	108	72
$[\text{MeMg}(\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe})]_2$ ^c	2.932	2.10 Mg—C (term) 2.10 Mg—N (bridge)	—	88.3 (Mg—N—Mg)
$\text{Mg}(\text{Me})\text{Br} \cdot 3\text{THF}$ ^d	—	2.41	—	—
$\text{Mg}(\text{Ph})\text{Br} \cdot 2\text{Et}_2\text{O}$ ^e	—	2.2	—	—
$\text{EtMgBr} \cdot 2\text{Et}_2\text{O}$ ^f	—	2.16	—	—
$\text{Me}_2\text{Mg}(\text{NC}_7\text{H}_{13})_2$ ^g	—	2.24 2.163	—	—
$(\text{EtMg}_2\text{Cl}_3 \cdot \text{THF}_3)_2$ ^h	—	2.19	—	—
$\text{CpMgBr} \cdot 2\text{NEt}_3$ ⁱ	—	2.55 h=2.21	—	—

^a Reference 123.

^b Reference 124.

^c Reference 73.

^d M. Vallino, *J. Organometal. Chem.* **20**, 1 (1969).

^e G. D. Stucky and R. E. Rundle, *J. Amer. Chem. Soc.* **86**, 4825 (1964).

^f L. J. Guggenberger and R. E. Rundle, *J. Amer. Chem. Soc.* **86**, 5344 (1964).

^g J. Toney and G. D. Stucky, *J. Organometal. Chem.* **22**, 241 (1970).

^h G. D. Stucky and J. D. Toney, *J. Organometal. Chem.* **28**, 5 (1971).

ⁱ C. Johnson, J. Toney, and G. D. Stucky, *J. Organometal. Chem.* **40**, C11 (1972).

tially from those previously discussed. The electronic configuration, with the severely limited number of available electrons and the increased availability of vacant orbitals, permits the element to enter into formation of three-dimensional cluster compounds or aggregates as compared to the simple dimeric or chain structures observed for the Group II and III derivatives.

The molecular weight data given in Table VII show that dimers, tetramers, and hexamers all exist in solution. It appears that under suitable conditions equilibria exist among these species,



with only small energy differences between the various species. These studies have been extensively reviewed along with all of the early structure work by Brown (20), while several authors (21, 81, 120) have reviewed both the chemistry and spectroscopic studies which have been reported for organolithium compounds.

The first observation which one can make is that the degree of aggregation for the alkyl derivatives is largely determined by the size of

TABLE VII
DEGREE OF AGGREGATION FOR SELECTED ORGANOLITHIUM
COMPOUNDS

Compound	<i>n</i>	Solvent
Menthyl lithium	2	Cyclohexane ^a
	2	Benzene ^a
Ethyl lithium	4	Gas phase ^b
	6	
<i>n</i> -Pentyl lithium	6	Cyclohexane ^c
	6	Benzene ^c
<i>n</i> -Octyl lithium	6	Benzene ^d
Trimethylsilylmethyl lithium	6	Cyclohexane ^c
Trimethylsilylmethyl lithium	4 ^e	Benzene ^c
<i>t</i> -Butyl lithium	4	Cyclohexane ^c
Isopropyl lithium	4 ^f	Cyclohexane ^c
		Benzene

^a Reference 45.

^b Reference 17.

^c Reference 67.

^d D. Margerison and J. D. Pont, *Trans. Faraday Soc.*, Part 2, 353 (1971).

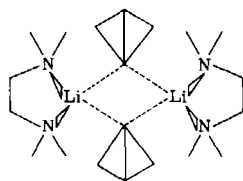
^e With increasing concentrations, the degree of association approaches 6.

^f With increasing concentration, the degree of aggregation increases.

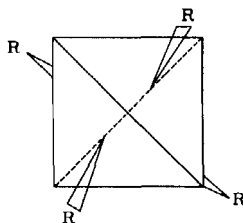
the bridging group. This is shown in the progression: (menthyllithium)₂ (45) < (*t*-butyllithium)₄ (67) < (ethylolithium)₆ (67) in hydrocarbon solvent. The menthyl group is so large that it cannot occupy the area above a triangular face on either the tetrameric or hexameric lithium cluster, thus preventing formation of higher aggregates. This is shown on detailed examination of *t*-butyllithium, where it has been shown by a minimum energy calculation that the *t*-butyl group fully covers the face of the lithium tetramer. In fact, these calculations show that the lithium-carbon distances must be elongated by the repulsion between *t*-butyl groups (103). Unfortunately, a crystal structure of this species has not been reported and one cannot test the calculations by experiment. For cases where less crowding occurs, e.g., where the R group has fewer α substituents, the aggregate size increases to hexamer. This occurs in the ethyl and *n*-butyl case, as well as in many others where somewhat more crowding occurs, as in *sec*-butyl or in trimethylsilylmethylolithium (67). A further indication of the steric effect is given by examination of trimethylsilyllithium which has the same substitution as *t*-butyllithium but a greater Si—Li distance, permitting formation of higher aggregates (101).

A. Structural Studies on Organolithium Compounds

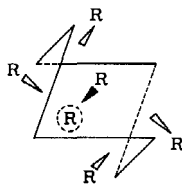
Three structural types [XXII (74), XXIII (125, 126), and XXIV (101, 134)] for organolithium compounds have been observed by X-ray



(XXII)



(XXIII)



(XXIV)

crystallography. Structure XXII is that of a dimeric species with what might be considered more normal electron-deficient bridge bonds. It occurs in this form as a result of the coordination of the tetramethylethylenediamine molecules to the lithium atom, thus reducing the number of orbitals available for use in multicentered bonding to a set equivalent approximately to those available in Al_2Me_6 , and yields a similar dimeric structure with a four-coordinate metal atom. The menthyllithium previously mentioned is presumably dimeric because of steric crowding and will have a far different electronic configuration due to the additional vacant orbitals present on the lithium center.

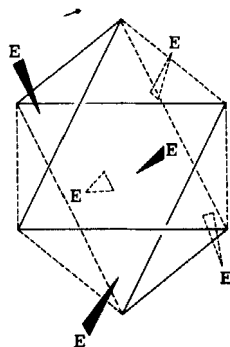
The other structures all represent cases in which the Group IV element is interacting with 3 lithium atoms, and in each case a three-dimensional lithium aggregate is formed. The lithium-lithium and lithium-carbon distances are summarized in Table VIII for those structures that have been determined. In addition, lithium-carbon distances in several lithium-aromatic ion pair systems are included in Table VIII for comparison (18, 19), as well as the observed distances in the hexamer of trimethylsilyllithium. In the dimeric molecule, the Li—Li distance of

TABLE VIII
STRUCTURAL PARAMETERS FOR LITHIUM DERIVATIVES

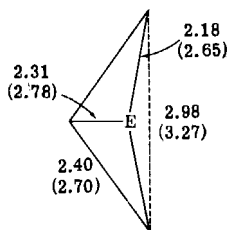
Compound	Li—Li (Å)	Li—C (Å)	Li—C—Li (°)	Ref.
$(\text{Li} \oplus)_2\text{TMEDA}^a$	2.74	2.23	76	135
$(\text{LiMe})_4$	2.68	2.31	68.3 ± 0.2	124, 125
$(\text{LiEt})_4$	2.424 ± 0.009	2.188	66.1 ± 0.2	36
	2.603 ± 0.010	2.252	66.7 ± 0.2	36
	2.633 ± 0.008	2.468	63.1 ± 0.2	36
$(\text{Li}-\text{c}-\text{C}_6\text{H}_{11})_6$	2.41	2.184 (avg.)	—	133
	2.40	—	—	133
	2.98	2.300	—	133
$(\text{LiSiMe}_3)_6$	2.70	2.68 (Si)	—	101
	3.27	—	—	101
Triphenylmethyl- lithium·TMEDA	—	2.23 C(1)	—	18
		2.49 C(14)	—	18
		2.54 C(15)	—	18
		2.51 C(2)	—	18
Bis[TMEDA lithium (1)] naphthalenide	—	2.32 C(1)	—	19
		2.27 C(2)	—	19
		2.26 C(3)	—	19
		2.33 C(4)	—	19
		2.66 C(5)	—	19
		2.66 C(5')	—	19

^a Bicyclo[1,1,0]butan-1-yl lithium TMEDA.

2.74 Å is approximately twice the observed covalent radius of lithium, and both the Li—C distance and the Li—C—Li angle are reminiscent of the trimethylaluminum structure previously described. In the two tetramers for which structural data are available, the Li—Li distances are substantially shorter in the range of 2.4 to 2.6 Å with Li—C distances in the 2.2–2.5 Å range. Crystallization effects may play a substantial role in the ethyllithium system since this compound is hexameric in noninteracting solvents but crystallizes in the tetrameric form.



(XXVa)

Distance in cyclohexyllithium
and in (trimethylsilyllithium)

(XXVb)

Examination of the recently reported structure of the cyclohexyllithium hexamer (XXV) shows similar Li—C distances of 2.18 and 2.30 Å, but it has two very different Li—Li distances of 2.4 and 2.98 Å. In the trimethylsilyl hexamer, similar findings are observed (the numbers in parentheses, structure XXVb) but the Li—Li distances are now found to be 2.70 and 3.27 Å. In both cases, the long Li—Li distances are around the edges of the unoccupied face of the system with the short distances along two of the three edges of the six occupied faces.

B. Bonding in Organolithium Aggregates

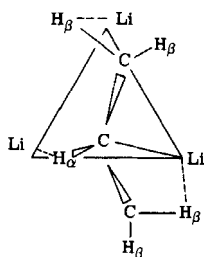
If we now attempt to discuss the bonding present within these systems, we find two possible views both of which have some support from experiment as well as some justification from theoretical calculations.

First, comparing the short Li—Li distances observed in all of these systems with twice the covalent radius of lithium, we find that appreciable interaction could occur. Further support for Li—Li interaction is provided by the observed mass spectral studies reviewed by Berkowitz (17), and certainly support comes from most of the theoretical calcula-

tions that indicate appreciable Li—Li interactions (31, 49, 89, 90, 92). Some experimental support for these results is provided by the examination of the spectral properties of these systems and by the prediction of the observed transitions from the theoretical calculations (107a).

The second view, namely that bonding is through the Group IV atom with essentially no metal-metal interaction, has been supported by Raman spectral studies that were interpreted for *t*-butyllithium tetramer as indicating essentially no Li—Li interaction (104). Additional evidence for this position comes from the failure to observe ^6Li — ^7Li coupling (22a); but this failure to observe coupling can also be accounted for by the fact that the orbitals which would be used in an Li—Li bond are predominantly made up of p atomic orbitals and, thus, would not provide appreciable coupling if the Fermi contact mechanism predominates (103). Possibly the strongest argument for limited or no Li—Li interaction comes from a recently reported EPR study of the free radical $(\text{LiR})_4$ (25), indicating that the electron only interacts with the CH_2 on the carbon and with 3 of the 4 lithium atoms in the tetramer, despite theoretical calculations that would suggest substantial hyperfine coupling with the fourth atom as well.

In summarizing these arguments, it is obvious that the question still remains open and awaits clarification by further study.



(XXVI)

A final possibility to be discussed is the proposal of Craubner (32), recently supported by Stucky *et al.* (134), in which it was suggested that Li—H interactions play a major role. It was proposed that in cyclohexyllithium the stereochemistry is determined in large part by Li—H interactions which are shown in the projection of a portion of the cyclohexyl group on to the face of the lithium aggregate (XXVI). These interactions involve both the α - and β -hydrogens of the cyclohexane ring and appear to determine its orientation. However, the observed Li—H distances are all greater than 2 Å, which is a long distance for the interaction of hydrogen. Further, one might note that in species such as *t*-butyllithium or trimethylsilyllithium (101), no α -hydrogens exist, and,

because of the steric requirements of the group, only limited interaction could occur with the β -hydrogen atoms.

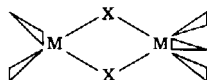
It, therefore, seems probable that the suggested Li—H interactions do not always have any appreciable effect on the stability of the lithium aggregate, even though they may have some influence on the conformation adopted by the cyclohexyl ring in cyclohexyllithium hexamer or in other selected cases.

VII

ELECTRON-DEFICIENT BRIDGE BONDS BETWEEN UNLIKE METAL ATOMS

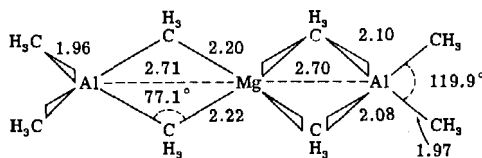
A. Mixed Group II—Group III Derivatives

There are a substantial number of systems in which electron-deficient bridge bonds have been reported to occur between dissimilar metals, e.g.,



(XXVII)

In general, these are derived from combinations of two of the species already discussed which form electron-deficient bridge bonds such as derivatives of aluminum and magnesium. In the structure of one of these derivatives (XXVIII), we see that the magnesium assumes a central position and is bridged symmetrically to aluminum atoms via methyl bridging groups (14). We again should examine the metal-metal and metal-carbon distances. Here we find that the Al—Mg distance is 2.70 Å with an Al—C bridging distance of 2.10 Å and an Mg—C distance to the same atom equal to 2.20 Å. These distances and angles in XVIII are very similar to those observed for the Al—C bridge distances (Table II) and to the Mg—C distances found for bridging carbons (Table VI). The metal-metal distance is about the average of the metal-metal distances



(XXVIII)

observed in the two types of bridged derivatives. Recent NMR evidence suggesting that they have reasonable stability has been reported for some of these species in solution (77).

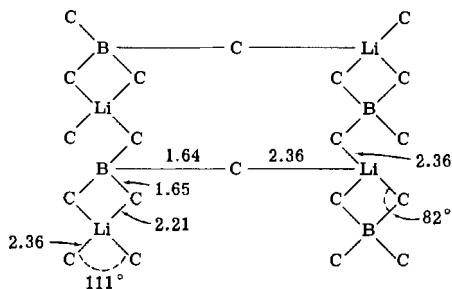
A similar derivative has been proposed on the basis of spectral studies on a mixture of BeMe_2 and AlMe_3 , but this derivative appears to be far less stable (14). This is thought to be the result of steric interactions that occur between the bridge and terminal groups. It also may be in part a result of poor metal-metal interaction in this type of system, but, as suggested earlier, this is a very speculative point.

Although little work has been reported in this area, it seems very probable that many such compounds will be found in which magnesium and possibly beryllium will be bound to aluminum via electron-deficient bridges. Compounds that would be of obvious interest from a structural point of view would be those with phenyl, ethynyl, vinyl, and cyclopropyl bridging groups to determine the nature of the interaction between these known strong bridging groups and all the possible different metal environments resulting from the introduction of two different metal atoms in the same system.

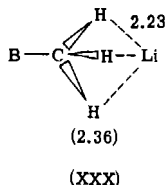
B. Lithium Alkyl-Group III Metalates

Let us now focus our attention on the interaction between lithium alkyls and Group III derivatives. These species are often considered to be metalates with discrete MR_4^- ions present, but a variety of studies show that substantial metal-anion interactions occur both in solution and in the solid state (45, 96, 131). More thorough examination of both of the structures and spectroscopic properties of these derivatives shows that they must be included in any treatment involving electron-deficient bonding.

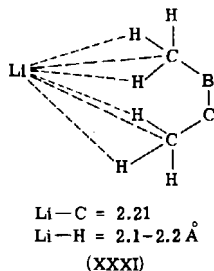
The structure of LiBMe_4 (the only boron compound to be specifically dealt with in this review) contains the shortest reported $\text{Li}-\text{C}$ bond in the literature (48, 95). The structure of this compound (XXIX) should be



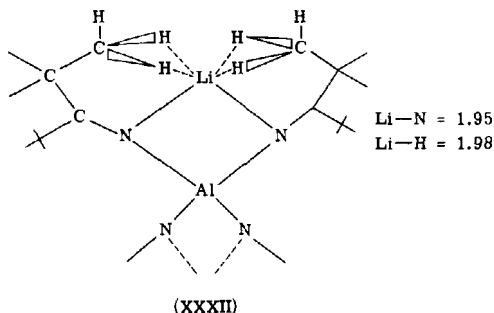
compared with the corresponding distances given in Table VIII. Clearly, both Li—C distances observed in this compound are of the same order of magnitudes as those observed in the bridged or aggregate organolithium compounds. The unique feature, however, is that one of the interactions has the B, C, and Li in a linear arrangement (XXIX and XXX) which requires that the hydrogen atoms are relatively close to the



lithium atom. Rhine *et al.* (95) have interpreted this in terms of Li—H interactions, as shown in XXX, and suggest the same interaction occurs in both interaggregate interaction in methyllithium and intramolecularly in the cyclohexyllithium as mentioned previously. They also suggest that hydrogen—lithium interactions are of major importance for the second type of Li—C—B bridging (XXIX and XXXI). Support for this type of

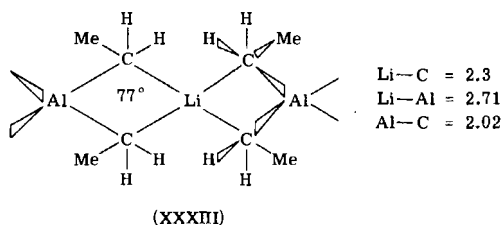


hydrogen bonding was said to come from the structure of $\text{LiAl}(\text{N}=\text{C}-t\text{-Bu})_4$ in which the lithium is surrounded as indicated in structure XXXII (107). Although these relatively short bonds may have some influence on the preferred conformations in the solid state, the



relatively long Li—H distances (2 Å or greater) and the other steric requirements of the substituents suggest to this author that this Li—H interaction is more an artifact of the overall geometric requirements of the groups involved and of crystal packing than of Li—H bonding.

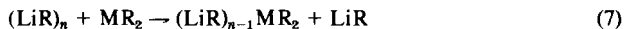
Considering now the other group III "ate" derivatives, we find that for LiAlEt_4 (XXXIII), one can again visualize Li—C bonding (44) taking place between the lithium and carbon atoms. In this instance no suggestion has been made that the species is stabilized by bridging hydrogen atoms.



For the heavier Group III metalates, essentially no bridging occurs; the reported species are said to have isolated anions for the sequence of compounds Li, Na, K, Rb, and CsInMe_4 (55). As an indication of the limited interaction, the Li—C distance is 2.448 Å—somewhat greater than that normally observed in compounds containing substantial Li—C bonding.

C. Lithium Alkyl-Group II Complexes

The reaction of $(\text{LiR})_n$ with Group II metal alkyls also would be expected to yield metalates but, in this instance, several products may be obtained as opposed to the rather simple reactions of Group III derivatives. The following reactions have been proposed:

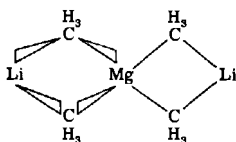


In each of these cases, we might expect some type of electron-deficient bonding, but only limited data are available relating to this problem.

It has been shown that $\text{LiMe} + \text{BeMe}_2$ forms the complex Li_2BeMe_4 , and the structure of this species has been determined (128). In this case the shortest Li—C distance is 2.52 Å, and it has been suggested that no appreciable Li—C bridging occurs. Similarly, the structures of Li_2ZnMe_4 (129), of $\text{K}_2\text{Zn}(\text{C}\equiv\text{CH})_4$ (127), and of $\text{K}_2\text{Cd}(\text{C}\equiv\text{CH})_4$ (127)

have been reported not to show electron-deficient bonding. The lithium silylmercurate, $\text{Li}_2\text{Hg}(\text{SiMe}_2\text{Ph})_4$ (3) has the lithium entrapped within a cage made up of carbon, silicon, and mercury atoms, but there is no clear indication of electron-deficient bond formation while in $\text{Li}_2\text{Hg}(\text{SiMe}_3)_4$ (56), the lithium atoms serve as bridges between the $\text{Hg}(\text{SiMe}_3)_4$ units forming an infinite chain.

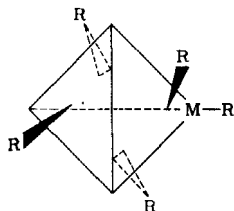
It has been suggested from NMR studies on solutions of Li_2MgMe_4 that species such as structure XXXIV are formed with possible formation of electron-deficient bridge bonds (22).



(XXXIV)

Examination of the 1 : 1 mixtures has shown the formation of crystalline LiMgPh_3 (132), $\text{LiHg}(\text{SiMe}_3)_3$ (101), and of $\text{Na}_2\text{Be}_2\text{H}_2\text{Et}_4$ (1) and $\text{Na}_2\text{Zn}_2\text{Et}_6$ (52) in which electron-deficient bond structures have been proposed (28). Unfortunately, none of these have been determined and are, therefore, only speculative.

In the same vein, reports have appeared suggesting the formation of 3 : 1 lithium-to-metal alkyl complexes (XXXV) with a structure resem-



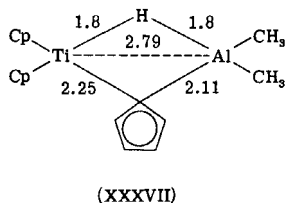
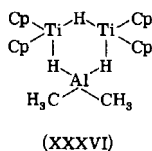
(XXXV)

bling that of the parent lithium alkyl (105). No definitive structural studies have appeared, but NMR data support the proposed structure and indicate that a variety of complexes of this type might be observed when further studies are carried out on beryllium, magnesium, zinc, and possibly other Group II metal alkyl derivatives.

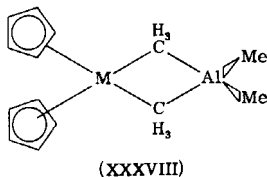
D. Electron-Deficient Bridged Main Group to Transition Metal Derivatives

Finally, it seems reasonable to speculate about structures that involve both a main group element and a transition element bound through

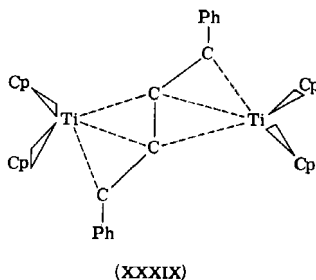
electron-deficient bonds. In this case, we again have only a few well-documented examples, two of which are structures XXXVI (50) and XXXVII (114). In both cases, we see hydrogen-bridging atoms, but in



XXXVII we also see a bridging group with Al—C distances very close to that observed in other bridged aluminum compounds. The distance between the metal centers in this compound is similar to that observed in the simpler aluminum derivatives but greater than the sum of the covalent radii of the two metals (2.54 Å), which may be an indication that Ti—Al interactions do not increase the stability of the bridged system. Structures on $\text{Cp}_2\text{MMe}_2\text{AlMe}_2$ ($\text{M} = \text{Y}, \text{Er}, \text{and Yb}$) have been recently completed and clearly show stable electron-deficient bonds between the aluminum and the transition metal moiety (XXXVIII) (12).



Similarly, the same workers have investigated the structure of $(\text{Cp}_2\text{YbMe})_2$ and shown that the two ytterbium atoms are bound by methyl bridges (12). In a related study, the dimeric titanium species $\text{MeCp}_2\text{TiC}_2\text{Ph}$ was prepared, but instead of having simple electron-deficient bridge bonds, the compound was shown to couple the two phenylethynyl groups leading to a product with the bridging unit shown in structure XXXIX (106).



This general area, namely the formation of electron-deficient bridged species involving main groups and transition metals or between two transition metals, is of major importance since many of these systems are involved in both homogeneous and heterogeneous catalysis systems. It seems likely that this area will lead to many studies in the future that should aid greatly our understanding both of the catalytic processes and of the requirements for electron-deficient bonds.

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Organometallic Radical Anions

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I

INTRODUCTION

A. Scope

In the most general sense, any anion radical produced by reduction with a metal, or by electrolytic reduction in the presence of a metallic counterion could be considered an organometallic anion radical. Any review based on such a definition would be monumental. To achieve a manageable volume of material, with a content suitable to the context of this series, we have limited this chapter to anion radicals produced from organometallic compounds. Anion radicals for which the metal is present solely as the reducing agent or counterion have, for the most part, been excluded.

An attempt has been made to cover the literature through the end of 1975, with primary emphasis on the results appearing in the last 10 years. We acknowledge the assistance of many workers in the field who shared preprints and unpublished results from theses with us.

There are a number of recent reviews that cover the earlier literature in the area of radical anions and complement the material in this chapter. Among the areas covered are radical anion intermediates in organic

chemistry (71), reactions of radical anions and dianions of aromatic hydrocarbons (70), electron transfer in naphthalene radical anions and alkyl halides (59), the chemistry of radical ions (128), ions and ion pairs (electron-exchange phenomena) (129), Group IV organometallic radicals and radical ions (132), Group IV radical reactions (76), inorganic hydrogen- and alkyl-containing free radicals (57), and anion radical polymerizations (58). The ESR hyperfine splitting constants for ion radicals in solution which were reported prior to midsummer, 1964, have been tabulated (12).

B. Definitions and Abbreviations

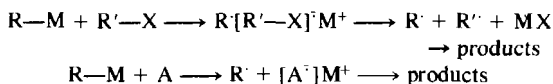
Throughout this review are tables giving ESR data which have been reported. Where the original report was explicit, the conditions of the observations are listed as: reducing agent/solvent(s), temperatures. The following abbreviations are used for the solvents: DG = diglyme; DME = 1,2-dimethoxyethane; DMF = *N,N*-dimethylformamide; HMPA = hexamethylphosphoramide; MeCN = acetonitrile; Me₂O = dimethyl ether; MTHF = 2-methyltetrahydrofuran; THF = tetrahydrofuran. For reducing agents, *e*⁻ indicates electrolytic reduction. The notation NaK indicates the use of sodium-potassium alloy, whereas Na,K indicates that either sodium or potassium was used as the reducing agent. The notation AM indicates Li, Na, K, Rb, Cs.

II

GROUPS I, II, AND III

A. Electron Transfer Processes

One-electron transfer processes are rather common in the reactions of Group I and II organometallic reagents with substrates, including alkyl halides, R'-X, and unsaturated organic acceptors, A (113):



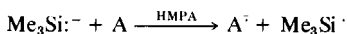
Such processes have been recognized when the donor organometallic, R-M, is a radical anion, a dianion, an alkyllithium reagent, or a Grignard reagent (113, 71, 70, 59, 114). In most cases, the anion radical

produced by the initial electron transfer is of extremely transitory existence, and its intermediacy can only be inferred from products, or from chemically induced dynamic nuclear polarization (CIDNP) observed during the reaction (136, 94). Occasionally, for the more stable anion radicals, direct observation of their ESR spectra has been possible (114).

It has been observed that *n*-butyllithium, phenyllithium, or benzyllithium react with sterically hindered olefins, such as 1,2,3,4-tetraphenylbutadiene, or tetraphenylethylene to form olefin radical anions. The electron-transfer only occurs in polar solvents such as THF, and in benzene there is no reaction (134). Transient alkyl radicals have been observed directly by ESR using a flow system in the reaction of alkylolithium reagents with a variety of alkyl halides (55). The lithium salts of radical anions of polycyclic aromatic hydrocarbons have been prepared under photolytic conditions using methylolithium, vinylolithium, or phenyllithium as the reducing agents (141). Evidence has recently been presented seeming to indicate that the conjugate addition of lithium dialkylcuprates with α,β -unsaturated carbonyl compounds involves initial one-electron transfer to give radical anion intermediates (72).

Some interesting electron-transfer reactions of sodium naphthalide have recently been reported. Reaction with phenylmercuric chloride or benzylmercuric chloride gives better than 70% yields of the symmetric diphenyl- or dibenzylmercury compounds. Solutions of alkali metals in HMPA lead to the same results (88). Evidence for the reaction of sodium naphthalide with methylene halides to give methylene anion radical, $\text{CH}_2^{\cdot-}$, has recently appeared (22).

Sakurai and co-workers (115, 116) have found that trimethylsilylsodium is an excellent one-electron transfer reagent in HMPA or other highly polar solvents:



The trimethylsilyl radical produced either rapidly dimerizes or reacts with solvent so that very clean ESR spectra of the radical anion, with minimum interactions with the counterion, can be obtained (116). Further reduction to dianions is very slow, and exhaustive reduction to anion radicals minimizes problems associated with exchange between anion radicals and unreduced substrate (115). It now appears that the solvent HMPA greatly facilitates the one-electron reduction, not only for trimethylsilylsodium, but also for organolithium and magnesium reagents (110). It was found that 0.1F solutions of methyl-, *n*-butyl-, or *t*-butyllithium or benzylmagnesium chloride will quantitatively reduce biphenyl to its radical anion in less than 10 minutes (110).

Ketyl radicals have been observed in the reactions of Grignard reagents with aromatic ketones (103). Similarly, reactions of Grignard reagents with the chelate, nickel(II) 3,5-diisopropylsalicylate, give rise to ketyl anion radicals (126).

B. *Properties of Anion Radicals*

The reviews cited in Section I, A summarize most of the properties of the radical anions of the Group I, II, and III metals.

In the reduction of conjugated dienes *cis* 1,4-addition of trimethylchlorosilane to give *cis*-1,4-bis(trimethylsilyl)-2-butene is favored with sodium in THF, lithium naphthalide in THF, and with lithium in diethylether. It appears that the anion radical, which in nonionizing solvents should exist in a *cis* configuration, leads to the *cis* 1,4-addition of the silyl groups, whereas the dianions produced by further reduction lead to *trans* products (140).

The ESR spectra of a series of triarylboron anion radicals have been determined and show selective line-broadening effects (95). The radical anions of diborane, generated in an argon matrix at 77 K by irradiation with α -rays have been studied by ESR (121). The vanadium-aluminum complex obtained on mixing dichlorobis(π -cyclopentadienyl)vanadium with ethylaluminum dichloride, a system that catalyzes the polymerization of ethylene to give a polymer with good characteristics, has been characterized by ESR and ultraviolet studies (44).

III

GROUP IV ELEMENTS

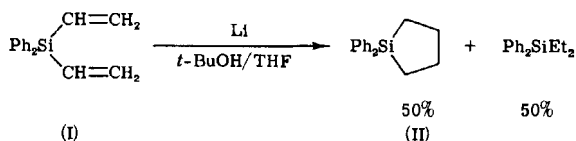
A. *Alkenyl and Alkynyl Derivatives*

1. *Preparation and Reactions*

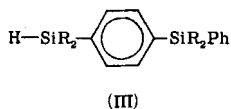
Alkenyl and alkynyl derivatives of the Group IV elements react readily with alkali metals at low temperatures in donor type solvents to give radical anions. With the exception of a few vinylsilicon (61) and alkynyl silicon and germanium radical anions (42, 43, 45) of sufficient stability to be observed spectroscopically at low temperatures, these anion radicals typically undergo two general types of reactions: coupling (polymerization), common for silicon and germanium derivatives (33); or

cleavage (devinylation), common for tin derivatives (33, 117). For the series of compounds $\text{Ph}_3\text{M}-\text{CH}=\text{CH}_2$, $\text{M} = \text{Si}, \text{Ge}$ and Sn , the electron affinity of the vinyl groups appears to decrease in the order $\text{Si} > \text{Ge} > \text{Sn}$, whereas the ease of cleavage of the $\text{C}-\text{M}$ bond increases in the order $\text{Si} < \text{Ge} < \text{Sn}$. This is consistent with the increasing electropositive character of the metal and with the relative strengths of the $\text{C}-\text{M}$ bonds in the series (34).

Vinyl silanes undergo reactions with alkali metals typical of arylenes and 1,3-butadienes (14), reductive dimerization or polymerization. Thus, for example, treatment of triphenylvinylsilane with one equivalent of lithium metal in THF solution at -75° , gives a 62% yield of 1,4-bis(triphenylsilyl)butane. Under similar conditions alkylvinylsilanes gave styrene-like polymerization (31). Electron spin resonance studies indicated the presence of very short-lived radical anion intermediates in these reactions (35), and controlled coupling could be achieved by chemical quenching of the anionic intermediates through the slow addition of a mixture of the vinylmetallic and *t*-butylalcohol to a slurry of one equivalent of lithium metal in anhydrous THF at -75° (33). Under these conditions, diphenyl(divinyl)silane (I) gave a 50% yield of 1,1-diphenylsilacyclopentane (II) along with diethyl(diphenyl)silane:

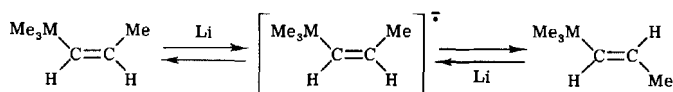


Reduction of I with potassium in DME containing 2% HMPA at -70° or lower gave an ESR spectrum attributed to the radical anion of II with one of the phenyl rings reduced (35). The coupling constants reported for this species, one ($a = 7.1$ G), two (1.95 G), and two (1.55 G) protons, are closer to those usually observed for an unsymmetrical species of type III,

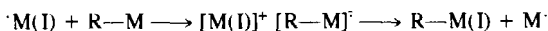


than to those typical of monosilylated benzenes (cf. Section III, B, 1). The ESR spectra attributed to species of type III were observed by the same workers when triphenyl(vinyl)silane or triphenylsilyl-1-propene were reduced (35). Interestingly, the reduction of 1-triphenylsilyl-1-propyne gave rise to an ESR spectrum ascribed to the triphenylsilylallyl radical, which requires proton abstraction from the solvent and rearrangement for its production (35).

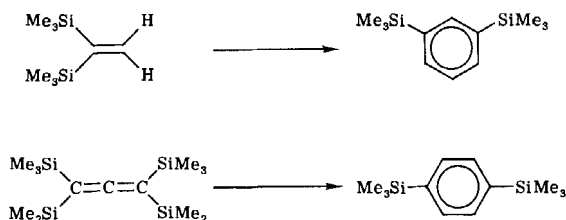
The site of bimolecular coupling in vinyl silanes of the type $R_3Si-CH=CHR'$ varies with structure. Triphenyl(vinyl)silane and triphenyl-(1-propenyl)silane undergo coupling at the carbons β to silicon, whereas trimethyl(*trans*- β -styryl)silane couples at the carbons α to silicon, consistent with the anticipated relative stabilization of the intermediate radical anions (33). Similar reactions are observed for triphenyl(vinyl)germane, but some Ge-vinyl bond cleavage occurs to give triphenylgermane. With triphenyl(vinyl)tin, exclusive Sn-vinyl bond cleavage is observed (33). These observations are all consistent with earlier suggestions that the isomerization of propenyl derivatives of tin, silicon, and germanium, induced by lithium, involve radical anion intermediates (117):



It was suggested further that the displacement of less electropositive metals from vinylmetallics by alkali metals involves initial electron transfer to produce an intermediate radical anion, followed by migration of the organic group to the reagent metal (117):

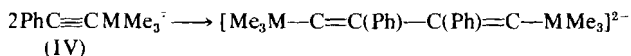


Coupling reactions have also been observed in the reduction of vinyl silanes with potassium in DME at low temperatures. Although reduction of *trans*-1,2-bis(trimethylsilyl)ethylene or 1,1,2-tris(trimethylsilyl)ethylene gives rise to radical anions detectable by ESR, the reduction of 1,1-bis(trimethylsilyl)ethylene gives rise to an ESR spectrum attributed to the radical anion of 1,3-bis(trimethylsilyl)benzene, and reduction of tetrakis(trimethylsilyl)allene gives rise to the spectrum of 1,4-bis(trimethylsilyl)benzenide (61). These reactions clearly must involve both reductive coupling and Si-C bond cleavage in the initial radical anions:



Alkynyl Group IV compounds of type IV ($\text{M} = \text{C}, \text{Si}, \text{Ge}$) may be reduced using any of the alkali metals in THF to give radical anions which, with the exception of $[\text{PhC}\equiv\text{CGeMe}_3]^\cdot \text{Li}^+$, are stable at -90° .

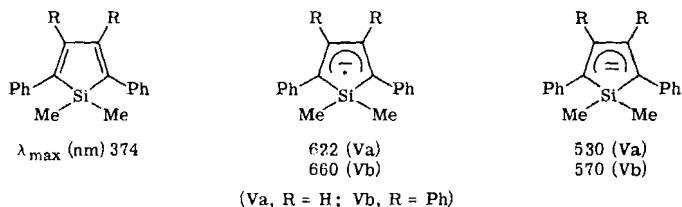
The radical anions have been characterized by their ESR spectra which have been assigned using deuterium labeling (45). Above -90° , the radical anions undergo a dimerization reaction (42, 45).



The radical anion of β -trimethylsilylstyrene also undergoes dimerization but coupling takes place at the carbons α to silicon (33). The kinetics of the alkyne dimerization, followed by ESR, showed the reaction to be second order in radical anion (43). With Li^+ , Na^+ , K^+ , or Rb^+ as the counterions, the rate increases in the order $\text{Si} < \text{C} < \text{Ge}$ (45). Consistent with the increased stability of the trimethylsilyl-substituted radical anion, the radical anion of 1,4-bis(trimethylsilyl)butadiyne, produced by reduction with Li, Na, K, Rb, or Cs in THF is stable at room temperature even on exposure to air, whereas the carbon analog, 1,4-di-*t*-butyl-1,3-butadiyne radical anion, dimerizes by second-order kinetics at -40° (42). The enhanced stability of the trimethylsilylalkynyl radical anions has been attributed to p-d π interactions (42).

2. Properties

Reduction of the silacyclopentadiene derivatives (Va and b) with potassium in DME proceeds through the radical anion to the di-

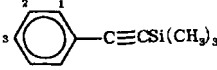
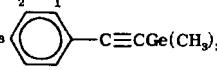
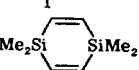
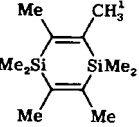
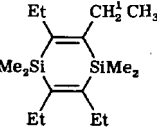


anion, which give the absorption maxima shown (79). Oxidation of the anion radical or dianions of structures V or several other silicon-containing heterocyclic radical anions gives chemiluminescence with moist oxygen (82) or with benzoyl peroxide, for which it was established that the emitter was the parent compound (77). In ENDOR experiments on radical anions of type V in solution, temperature-dependent variations in line widths and positions were observed due to hindered rotation of the phenyl groups. Activation energies and entropies suggested that the major part of the potential barrier to rotation stems from π -conjugation effects (133).

Table I summarizes the available ESR data for Group IV alkenyl or alkynyl radical anions.

TABLE I
GROUP IV ALKENYL AND ALKYNYL RADICAL ANION ESR DATA

Anion radical	a_1	a_2	$a(^{29}\text{Si})$	$a(\text{CH}_3)$	a_{other}	Conditions	Ref.
$\begin{array}{c} \text{H} \quad \text{SiMe}_3 \\ \diagdown \quad / \\ \text{C}^1 = \text{C}^2 \\ / \quad \diagdown \\ \text{Me}_3\text{Si} \quad \text{H} \end{array}$	7.49	7.49	6.72	0.36	5.6(^{13}C)	K/DME, -80°	61
$\begin{array}{c} \text{Me}_3\text{Si} \quad \text{SiMe}_3 \\ \diagdown \quad / \\ \text{C}^1 = \text{C}^2 \\ / \quad \diagdown \\ \text{Me}_3\text{Si} \quad \text{H} \end{array}$	—	9.05	6.0 to 9.0	0.26(Si^1), 0.37(Si^2)	—	K/DME, -80°	61
$\left(\begin{array}{c} \text{H} \\ \diagdown \\ \text{C}^1 = \text{C}^2 \\ / \quad \diagdown \\ \text{Me}_3\text{Si} \quad \text{H} \end{array} \right)_2$	6.71	3.22	5.73	0.24	—	K/DME, -80°	61
$\begin{array}{c} \text{H}^2 \\ \\ \text{Ph}_2\text{Si} - \text{C}^1 = \text{CH}_2^1 \\ \\ \text{H}^1 \end{array}$ (from $\text{Ph}_2\text{SiC}\equiv\text{CCH}_3$)	9.52	4.96	—	—	—	K/DME, HMPA, -70°	35, 41
$[(\text{C}^1\text{H}_3)_3\text{SiC}\equiv\text{C}]_2$	(^{13}C)	—	—	—	(M^+)	THF, -80°	42
	~4.60	0.15	5.25	0.15	—	Li	42
	4.63	0.15	5.00	0.15	0.40	Na	42
	4.63	0.16	4.95	0.16	0.30	K	42
	~4.60	0.17	4.90	0.17	—	Rb	42
	4.50	0.17	4.20	0.7	4.10	Cs	42

	3.16	0.16	4.4	0.3	7.49(3)	Na or K/THF, -80°	43, 45
	3.20	0.1	1.67(Ge)	0.15	7.50(3)	AM/THF, -90°	45
	3.04	—	—	0.24	—	K/DME, -70°	80
	5.32	—	—	0.18	—	K/DME, -70°	80
	1.93	—	—	—	—	K/DME, -70°	80

(continued)

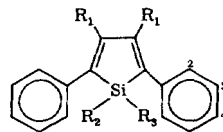


TABLE I—(Continued)

R ₁	R ₂	R ₃	a ₂	a ₃	a ₄	a(other)	Conditions	Ref.
H	Me	Me	1.46, 1.87	0.42, 0.56	2.25	3.17(R ₁), 0.13(CH ₃)	Na/MTHF, -103°	133
			1.51, 1.92	0.43, 0.58	2.32	3.25(R ₁), 0.13(CH ₃)	Na/MTHF, DG, -103°	133
Ph	Me	Me	1.29, 1.53	0.43, 0.53	1.86	—	Na/MTHF, DG, -98°	133
Ph	H	Me	1.31, 1.51	0.46	1.79	14.7(Si—H), 0.08, 0.22 ^a	Na/MTHF, DG, -91°	133
Ph	H	Ph	1.23, 1.44	0.45	1.74	14.4(Si—H), 0.05, 0.22 ^a	Na/MTHF, DG, -115°	133
Ph	Me	Ph	1.26, 1.47	0.46	1.80	0.16, 0.21 ^a	Na/DME, -99°	133
Ph	Ph	Ph	1.25, 1.46	0.45	1.70	0.08, 0.15, 0.21 ^a	Na/MTHF, DG, -93°	133

^a Unassigned.

B. Aryl Derivatives

1. Substituted Benzene Anion Radicals

a. Preparation and Reactions. Aryl Group IV derivatives are readily reduced in donor solvents using either alkali metals or electrochemical reduction. For silicon and germanium, the anion radicals have stability sufficient to allow detailed study and characterization. In the case of the tin and lead compounds, the instability of the radical anions has, for the most part, precluded definitive studies. Thus, for example, brief treatment of a solution of 4,4'-bis(trimethylstannyl)biphenyl in THF with sodium-potassium alloy at -63° , gives a pale green solution, which gives a five-line ESR spectrum with splittings of 2.36 G. The spectrum decays at higher temperatures to give another ESR spectrum, which is identical to that obtained from the decomposition of sodium biphenylide, clearly indicating the loss of the trimethylstannyl groups from the initial radical anion. Analogous silicon and germanium radical anions are stable at room temperature (20).

Group IV substituents, especially the trimethylsilyl group, apparently enhance the electron affinity of aromatic systems. The effect is particularly noticeable in aniline derivatives. The strong electron-releasing effect of the amino group decreases the electron affinity of the aniline derivatives and hinders reduction to the radical anions. Nitroanilines may be reduced to radical anions (65). The only other aniline radical anions that have been reported bear silyl substituents either at nitrogen (62) or on the ring (83, 85, 86).

Arylsilane radical anions undergo cleavage and coupling reactions, usually under conditions where excess reducing agent is available. Reduction of phenylsilane, diphenylsilane, or triphenylsilane with sodium-potassium alloy under preparative conditions gives high yields of tetraphenylsilane (7). In the reduction of phenylsilanes, the appearance of 1,4-bis(silyl)benzene radical anions is frequently observed (135, 35, 86, 97, 75, 120, 100). Typical results are shown in Table II.

In addition to coupling products, reductive coupling products that involve proton or methyl group abstraction from the reaction medium are observed. The radical anion of phenylpentamethyldisilane produced by reduction with potassium in dimethoxyethane is stable at low temperatures. On warming over -40° , loss of a trimethylsilyl group and gain of a hydrogen atom occurs to produce the radical anion of phenyldimethylsilane (61):

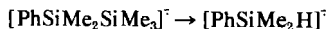


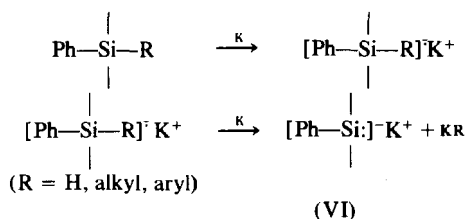
TABLE II
REDUCTIVE COUPLING PRODUCTS FROM ARYL SILANES

Starting phenyl silane	Anion radical ^a		$a_{\text{Si-H}}$	a_{aryl}	Conditions	Ref.
	R	R'				
Ph ₃ SiH	Ph ₃	HPh ₂	6.10	1.86	K/THF, -76°	135
	Ph ₃	Ph ₃		1.86		135
PhSiMe ₂ H	MePhH	HMe ₂	7.02	1.80	K/THF, -76°	135
	Me ₂ Ph	HMe ₂	6.28	1.88	K/THF, -76°	135
PhSiMeH ₂	MePhH	HPhMe	6.67	1.78	K/THF, -76°	135
Ph ₃ SiCH=CH ₂ or Ph ₃ SiCH=CHCH ₃	R ₂ H	R ₂ H	5.02	1.60	K/DME, HMPA, -70°	35
Ph ₂ SiR ₂ (R = Me, Et, Ph)	?	?	—	1.9–2.1	K/DME, THF, -70° to 20°	100
Ph ₂ SiR (R = Me, Et, Ph, OSiMe ₃)	?	?	—	2.1–4	—	97
<i>p</i> -MeH ₂ SiC ₆ H ₄ NMe ₂	Me ₂ H	Me ₂ C ₆ H ₄ NMe ₂	7.05	1.85	K/DME, THF, -76°	86
	Me ₃	Me ₂ C ₆ H ₄ NMe ₂	—	1.78	—	86
<i>p</i> -MeH ₂ SiC ₆ H ₄ NMe ₂	Me ₂ H—	MeC ₆ H ₄ NMe ₂	7.21	1.75	K/DME, THF, -76°	86
<i>p</i> -SiH ₃ C ₆ H ₄ NMe ₂	MeH ₂ Si	SiH ₂ C ₆ H ₄ NMe ₂	6.05	1.70	—	86
Ph ₃ SiCH ₃	Me ₃	Me ₃	—	1.65	K/DME, -70°	120

^a Tentative structures.

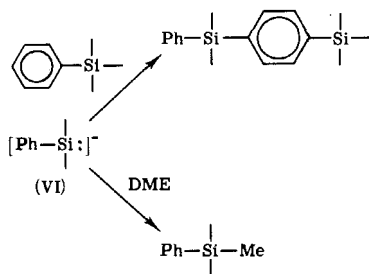
Similarly, 1-trimethylsilylmethyl-4-trimethylsilylbenzene leads to the radical anion of *p*-trimethylsilyltoluene (61). The metallic reduction of diphenyldimethylsilane, triphenylmethylsilane, or tetraphenylsilane in DME eventually gave the radical anion of phenyltrimethylsilane when the reductions were carried out in DME (135). This observation led to the suggestion that workers who reported that the radical anions of Ph_2SiMe_2 , Ph_2SiEt_2 (100), Ph_3SiMe , Ph_3SiH , and Ph_4Si (97) all involved localization of the unpaired electron in one phenyl ring (100, 97) were actually observing the ESR spectra of a trialkylphenylsilane radical anion (135).

It appears that these reactions all may be explained by invoking a common intermediate phenylsilyl anion (VI) formed from the initial radical anion by reductive cleavage of a silicon-hydrogen or silicon-carbon bond:



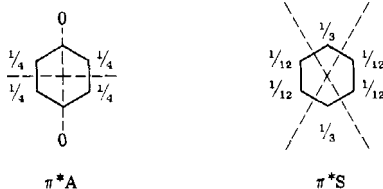
Comparison of all reported cleavages gives the apparent ordering $\text{H} > \text{Ph (or aryl)} > \text{alkyl}$ in terms of tendency for groups to be cleaved from silicon, with the exception that at least one aryl substituent is retained on silicon in the anion VI. It is clear that reduction of aryl silanes leads to significant weakening of Si—R bonds that have appropriate symmetry for hyperconjugative interactions with the reduced π systems, a point that has been cited as evidence for the importance of $\pi^* \rightarrow \sigma^*$ and $\pi \rightarrow \sigma^*$ type interactions in unsaturated silanes (86).

In subsequent reactions, the arylsilyl anion (VI) can react with other arylsilanes to give the 1,4-coupling product or with DME to give a methyl-substituted derivative that, under the reaction conditions, may be further reduced to new radical anions (135):



A further complication in the reduction of aryl Group IV derivatives is the formation of biphenyl radical anion (135, 100, 97, 20) or its derivatives (32). However, this reaction is not peculiar to organometallic radical anions but appears to be quite general for alkali metal reduction of phenylated compounds (135).

b. Properties. Table III summarizes reported ESR results for Group IV-substituted benzene anion radicals. Qualitatively the ESR results may be interpreted in terms of benzene molecular orbitals. In benzene radical anion, the unpaired electron is in an orbital that is a mixture of the two, degenerate, lowest unfilled orbitals, the antisymmetric (π^*A) and symmetric (π^*S),

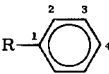


so that its average density on each carbon is 0.17. The ESR spectrum consists of seven equally spaced lines due to the six equivalent protons, and the hyperfine splitting constant is 3.75 G (6). The introduction of a substituent removes the degeneracy of the symmetric and antisymmetric orbitals. To a first approximation, an electron-releasing substituent should destabilize the symmetric π^* orbital, leaving the antisymmetric π^* orbital lowest in energy. The ESR spectrum of *t*-butylbenzene radical anion illustrates this condition, consisting of a basic quintet due to interaction of the unpaired electron with the four equivalent ortho and meta protons. A smaller splitting is observed for the para proton, probably due to some mixing of the symmetric state (6).

For all of the Group IV-monosubstituted benzene radical anions that have been reported the unpaired electron clearly occupies an orbital that is symmetric in character. Each compound shows a large hyperfine coupling constant for the para proton close to 8 G. The protons ortho to the point of metalloid substitution show the next-largest coupling, in the range of 2.5 to 3.0 G, whereas the meta protons show the smallest coupling. The observation of couplings for the methyl protons on silicon (135, 61, 6, 118, 122), for hydrogens on silicon (135, 61), and for the silicon-29 nucleus (61) gives evidence for spin delocalization to the silyl substituent.

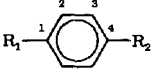
For the disubstituted Group IV anion radicals with alkyl substituents (61, 119), the strongly electron-releasing dimethylamino group (85, 84, 86), or other Group IV substituents (118, 61), the experimental results are consistent with the occupation of a symmetric-type molecular orbital

TABLE III
ARYL GROUP IV RADICAL ANION ESR DATA

A. Monosubstituted 							
R	a_2	a_3	a_4	$a(\text{M}-\text{CH}_3)$	$a(\text{other})$	Conditions	Ref.
H ₃ Si—	3.08	0.52	8.46	—	8.04(Si—H)	e^-/THF , DME, -76°	135
H ₂ MeSi—	2.76	0.64	8.40	<0.20	6.33(Si—H)	e^-/THF , DME, -76° or K/DME, -76°	135
HMe ₂ Si—	2.72	0.86	8.15	0.11	7.20(Si—H)	e^-/THF , DME, -76° or K/DME, -76°	135
Me ₃ Si—	2.70	0.97	8.12	0.13	0.81(Si—H)	K/DME, -80°	61
	2.66	1.06	8.13	0.40	—	NaK/DME, -50°	6
	2.65	1.06	8.09	0.26	5.18(²⁹ Si)	K/DME, -80°	61
	2.66	1.06	8.73	—	—	K/DME	122
	2.66	1.06	8.18	0.26	—	NaK/MTHF, DME, -70° to -80°	118
Me ₃ Ge—	2.61	1.05	8.06	0.26	—	K/THF, DME, -76°	135
	2.33	1.46	7.61	<0.10	—	NaK/DME, -50°	6
Me ₃ Si ₂ —	2.67	0.93	8.15	0.13(α -Si)	5.42(α -Si) 8.9(C-1) 10.8(C-4)	K/DME, -80°	61
	2.66	0.95	8.09	0.14	—	NaK/MTHF, DME, -70° to -80°	118
(Me ₃ Si) ₃ Si—	2.89	1.03	7.84	—	—	NaK/MTHF, DME, -70° to -80°	118
cyclo-Si ₈ Me ₁₁ —	2.65		7.65	—	—	e^-/THF , -95°	94
PhMe ₂ SiOMe ₂ Si—	2.7	1.0	8.5	—	—	K or Na/THF, DME, -70° to -40°	111
PhMe ₂ SiNHMe ₂ Si—	2.7	1.1	8.2	0.5	—	K/DME, -70° to -50°	97
	2.7	1.1	8.2	—	—	K/DME	97

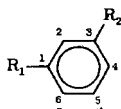
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TABLE III—(Continued)

B. Para-disubstituted 		a_2	a_3	$a(\text{M}-\text{CH}_3)$	$a(\text{other})$	Conditions	Ref.
$\text{Me}_3\text{Si}-$	$-\text{CH}_3$	3.25	1.47	0.20	8.43($p\text{-CH}_3$) 4.26(^{29}Si)	K/DME, -80°	61
		3.20	1.50	0.20	8.20($p\text{-CH}_3$)	NaK/MTHF, DME, -70° to -80°	119
$\text{Me}_3\text{Si}-$	$-\text{CH}_2\text{CH}_3$	3.21	1.38	0.24	6.02($p\text{-CH}_2-$)	NaK/MTHF, DME, -70° to -80°	119
$\text{Me}_3\text{Si}-$	$-\text{CH}(\text{CH}_3)_2$	3.39	1.27	0.24	4.83($p\text{-CH=}$)	NaK/MTHF, DME, -70° to -80°	119
$\text{Me}_3\text{Si}-$	$-\text{C}(\text{CH}_3)_3$	3.04	1.22	0.23	0.06[$\text{C}(\text{CH}_3)_3$] 4.67(^{29}Si)	K/DME, -80°	61
		3.40	1.23	0.24		NaK/MTHF, DME, -70° to -80°	119
$\text{Me}_3\text{Si}-$	CH_2SiMe_3	3.72	1.35	—	6.48($-\text{CH}_2-$)	NaK/MTHF, DME, -70° to -80°	119
$\text{H}_3\text{Si}-$	$-\text{NMe}_2$	3.94	1.59	—	5.35($\text{Si}-\text{H}$)	e^-/THF , -96°	86
$\text{MeH}_2\text{Si}-$	$-\text{NMe}_2$	4.02	1.78	0.20	3.81($\text{Si}-\text{H}$)	e^-/THF , -90°	86
$\text{Me}_2\text{HSi}-$	$-\text{NMe}_2$	4.07	2.39	0.18	3.08($\text{Si}-\text{H}$)	K/THF, DME, -90°	86
$\text{Me}_3\text{Si}-$	$-\text{NMe}_2$	4.55	3.25	0.15	—	K/THF, DME, -90°	85, 84
$\text{Me}_3\text{Si}-$	$-\text{NO}_2$	1.0	3.4	—	9.2(N)	e^-/DMF , 20°	90
		0.9	3.3	—	9.7(N)	e^-/MeCN , 20°	90
		1.0	3.5	—	9.8(10.4) (N)	K/DME, -70°	90
		~ 0.8	3.5	—	10.1 (N)	Na/DME, -70°	90
		~ 0.8	3.8	—	≈ 0.8 (Na)	Na/THF, -70°	90
$\text{Me}_2\text{HSi}-$	$-\text{SiHMe}_2$	1.78	1.78	—	7.28($\text{Si}-\text{H}$)	e^-/THF or K/THF	135

Me ₃ Si—	—SiMe ₃	1.83	1.83	0.27	0.09(K)	K/THF, -50°	1
		1.76	1.76	0.271	—	K/DME, -70°	2
		1.76	1.76	0.27	6.17(²⁹ Si)	K/DME, -80°	61
		1.77	1.78	0.27	—	NaK/MTHF, DME, -70° to -80°	118
Me ₃ Ge—	—C(CH ₃) ₃	3.38	2.23	—	—	NaK/MTHF, DME, -70° to -80°	119
Me ₃ Ge—	—GeMe ₃	1.88	1.88	—	—	K/THF, -50°	1

C. Meta-disubstituted



R ₁	R ₂	<i>a</i> ₂	<i>a</i> ₄	<i>a</i> ₅	<i>a</i> ₆	<i>a</i> (M—CH ₃)	<i>a</i> (other)	Conditions	Ref.
Me ₃ Si—	—CH ₃	2.60	8.09	1.06	2.60	0	1.06(<i>m</i> -CH ₃)	NaK/MTHF, DME, -70° to -80°	119
Me ₃ Si—	—C(CH ₃) ₃	2.46	8.04	1.68	2.46	0.28	—	NaK/MTHF, DME, -70° to -80°	119
Me ₃ Si—	—NMe ₂	4.25	7.35	2.67	0.78	0.23	—	K/MTHF, DME, -50°	85, 84
Me ₃ Si—	—NO ₂	3.6	3.6	1.1	4.0	—	9.7(N)	<i>e</i> ⁻ /DMF, 20°	90
		3.4	3.4	1.0	3.8	—	10.0(N)	<i>e</i> ⁻ /MeCN, 20°	90
		3.4	3.4	1.0	4.0	—	10.7(N)	K/DME, -70°	90
		3.3	3.3	1.2	3.8	—	10.5(N)	K/THF, -70°	90
		3.8	3.8	~1.0	4.0	—	10.8(N)	Na/DME, -70°	90
		3.6	3.6	~1.0	4.0	—	10.6(N)	Na/THF, -70°	90
Me ₃ Si—	—SiMe ₃	0.30	6.94	0.66	6.94	0.16	4.06(²⁹ Si) 9.3(¹³ C)	K/THF, -80°	61
		0.24	6.98	0.72	6.98	0.24	—	NaK/MTHF, DME, -100°	118
Me ₃ Ge—	—C(CH ₃) ₃	2.33	7.79	1.41	2.33	—	—	NaK/MTHF, DME, -70°	119

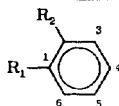
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TABLE III—(Continued)

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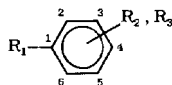
PAUL RONALD JONES

D. Ortho-disubstituted



R_1	R_2	a_3	a_4	a_5	a_6	$a(M-CH_3)$	$a(\text{other})$	Conditions	Ref.
Me_3Si-	$-CH_3$	0.4	8.1	0.4	2.8	0.4	2.8(<i>o</i> - CH_3)	K/DME	89 (sic)
		1.06	8.42	—	—	0.32	2.83(<i>o</i> - CH_3)	NaK/MTHF, DME, -70° to -80°	119
Me_3Si-	$-NMe_2$	1.72	8.48	0.50	3.60	0.26	—	K/THF, DME, -50°	85, 84
Me_2HSi-	$-NMe_2$	1.16	8.44	0.16	3.45	0.16	5.37(Si—H)	K/MTHF, DME, -80°	87
MeH_2Si-	$-NMe_2$	1.0	8.4	0.14	2.8	<0.1	6.1(Si—H)	K/MTHF, DME, -80°	87
Me_3Si-	$-SiMe_3$	0.46	5.23	5.23	0.46	0.23	4.48(^{29}Si)	K/DME, -80°	61
		—	5.4	5.4	—	—	—	K/DME, -75°	89

E. Polysubstituted



R_1	R_2, R_3	a_2	a_3	a_4	a_5	a_6	$a(M-CH_3)$	Conditions	Ref.
Me_3Si	2,6-diMe	3.10(CH_3)	0.87	8.31	0.87	3.10(CH_3)	0.22	NaK/MTHF, DME, -70° to -80°	119
Me_3Si	3,5-diMe	2.34	1.20(CH_3)	7.67	1.20(CH_3)	2.34	0.29	NaK/MTHF, DME, -70° to -80°	119
Me_3Si	2,4,6-triMe	3.10(CH_3)	0.87	8.30(CH_3)	0.87	3.10(CH_3)	0.20	NaK/MTHF, DME, -70° to -80°	119
Me_3Si	2- NMe_2 , 4-Me	—	2.23	9.11(CH_3)	0.42	4.72	0.18	K/THF, DME, -90°	85
Me_3Si	3- NMe_2 , 4-Me	4.75	—	8.89(CH_3)	2.67	0.74	0.20	K/THF, DME, -90°	85
Me_3Si	3,5-diMe $_3Si$	4.62	—	4.62	—	4.62	0.16	K/DME, -80°	61 (see also 37)

by the unpaired electron. The organosilyl and organogermyl substituents are, therefore, electron acceptor substituents, and the magnitude of their stabilizing effect on the symmetric π^* orbital is greater than the destabilizing effects of electron-releasing substituents (119, 84).

There are two cases where Group IV substitution results in stabilization and, hence, occupation of an apparently antisymmetric π^* orbital: the *m*- and *o*-bis(trimethylsilyl)benzene radical anions (61, 119, 89). These exceptions are qualitatively in accord with the prediction that meta or ortho substitution by electron-withdrawing substituents would favor stabilization of the antisymmetric π^* orbital (118). The electron-withdrawing effect of a nitro substituent is apparently greater than that of a trimethylsilyl group, for in both *p*-nitrophenyltrimethylsilane and *m*-nitrophenyltrimethylsilane radical anions the nitro group dominates the spin distribution (90).

2. Other Aromatic Systems

a. Polyphenylenes. The ESR spectra of a series of trimethylsilyl and trimethylgermyl biphenyl anion radicals (20) and polyphenylene systems (18, 1) have been reported and the results are summarized in Table IV. Increasing stability of the radical anions is observed with increasing length of the polyphenyl chain. The smaller, ring proton coupling constants for silicon compounds compared to the germanium compounds, and the larger couplings for the methyl protons of the trimethylsilyl group, indicate a larger spin density on silicon than on germanium and, thus, imply a stronger π -electron withdrawal by silicon relative to germanium (1). Nevertheless, bridging dimethylsilyl groups do not participate in "through conjugation" and separate apparently independent π -systems (18).

b. Naphthalene Derivatives. The available ESR data for trimethylsilyl and trimethylgermyl naphthalene radical anions, summarized in Table V, are again consistent with delocalization on to the metalloid atom (49, 61, 1).

c. Benzheterocycles. The radical anion of 5,5-diphenyldibenzosilole (VII; R = Ph) produced by reduction with potassium in DME, gives

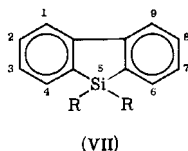
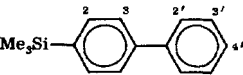
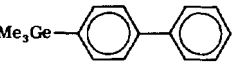
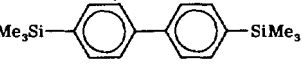
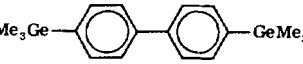
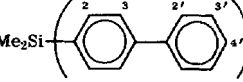
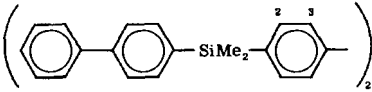
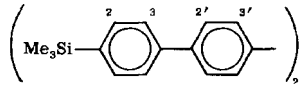
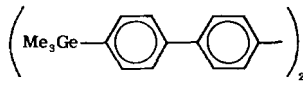
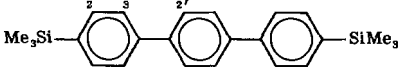
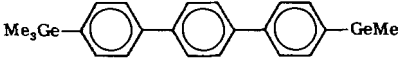


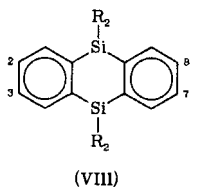
TABLE IV
GROUP IV POLYPHENYLENE RADICAL ANIONS

Anion radical	<i>a</i> (2)	<i>a</i> (3)	<i>a</i> 2'	<i>a</i> 3'	<i>a</i> 4'	<i>a</i> (CH ₃)	Conditions	Ref.
	0.16	2.08	2.72	0.48	4.96	0.16	Na/THF, -50°	20
	0.00	2.38	2.70	0.52	5.08	0.00	Na/THF, -50°	20
	0.14	2.24	—	—	—	0.14	Na/THF, -50°	20
	0.20	2.41	—	—	—	0.00	Na/THF, -50°	20
	0.20	2.08	0.48	2.72	4.96	0.10	Na/THF, -100° to 0°	18

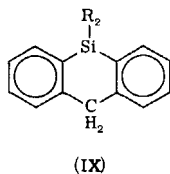
	0.14	2.20	[central biphenyl reduced]			0.06	Na/THF	18
		1.35	—	1.35	—	—	Na/THF	1
		1.32	0.32	1.32	—	—	NaK/THF	1
	0.32	1.83	0.90	—	—	0.08	Na/THF	1
	0.40	1.94	0.97	—	—	—	Na/THF	1

splittings $a_{3,7}^H = 3.1$, $a_{1,9}^H = 1.56$, $a_{2,4,6,8}^H = <0.3$ G (81) which are somewhat different from those obtained for the 5,5-dimethyl derivative (VII; R = Me), namely, $a_{3,7}^H = 4.0$, $a_{1,9}^H = 1.0$, $a_{4,6}^H = 0.8$, $a_{2,8}^H$ and $a_{Me}^H = 0.2$. The diphenyl derivative is more stable than the radical anion of its carbon derivative, 9,9-diphenylfluorene, but, after extended periods of reduction, the spectrum of the biphenyl radical anion begins to grow in intensity. The 5,5-dimethyl derivative appears to be stable under these conditions. The enhanced stability of the silicon derivative might be due to stabilization of the carbon-silicon bonds by delocalization of charge into available d-orbitals (81). Methyl proton hyperfine splitting observed for the anion radicals of the 5,5-dimethyl- and 5,5-diethyldibenzosilole has been cited as evidence for d- π interaction (36).

The ESR spectrum of 5,5,10,10-tetramethyl-5,10-dihydrosilanthrene radical anion (VIII; R = Me) produced by potassium reduction in DME



at room temperature consists of five lines, $a = 2.2$ G, assigned to the protons in the 2, 3, 7, and 8 positions, and a smaller coupling of 0.18 G attributed to the silicon methyl protons. At low temperatures, line-width alternation and broadening, observed in DME/THF solutions, were attributed to ion pairing, with the potassium counterion rapidly interchanging between locations close to the two silicons, where MO calculations predict the largest spin densities and charge occur (78). The explanation has been questioned by later workers who indicate that a large spin density on silicon should lead to a large, and unobserved ^{29}Si coupling (89). It is suggested that the radical actually being observed is a

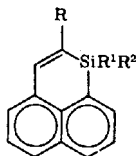


cleavage product of the original radical anion (89). It seems more likely to this author that the temperature variations in the ESR spectra of the

radical anion of VIII are due to electron exchange between the two aryl rings, as has been more recently observed by West and co-workers for diphenyldimethylsilane (91, 138). The system merits reinvestigation.

The attempted reduction of 9,10-disila-9,10-dihydroanthracene (VIII; R = H) led to immediate decomposition with the evolution of gas and an ESR spectrum due to several radicals including biphenyl radical anion. Similar results were obtained for 9-sila-9,10-dihydroanthracene (IX; R = H) (89). Reduction of 9,9-dimethyl-9-sila-9,10-dihydroanthracene (IX; R = Me) gave rise to an anion radical for which three unassigned couplings of 3.2, 2.6, and 0.7 G are reported (89).

The ESR data for several silaacenaphthene and silaphenalene radical anions (Table VI) obtained by electrolytic reduction (101), are similar to the results for trimethylsilyl-substituted naphthalenes (Table V) (49). The polarographic reduction potentials were 0.2–0.4 volt more positive than that of naphthalene (101). Similarly, some silaphenalene derivatives of the type X[R = H(R¹, R² = H, H; H, Me; Me, Me) and R = Ph; R¹ = R² = Me] were shown by polarographic analysis to reduce more easily than silylnaphthalene or naphthalene and the unassigned ESR spectra of the radical anions were reported (99).

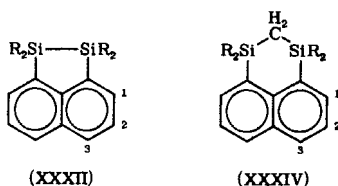


(X)

3. Electron-Exchange Phenomena.

The original report of the radical anion of tetraphenylsilane, produced by reduction with sodium or potassium in THF or DME at -70° , suggested that, on the basis of the odd number of lines obtained in the ESR spectrum, the unpaired electron was rapidly exchanging between the four phenyl rings of the molecule (131). The same paper indicated that for 4-biphenyltriphenylsilane radical anion the odd electron was localized almost exclusively on the biphenyl substituent (131). A subsequent report for tetraphenylsilane and a variety of other polyphenylsilyl radical anions, prepared by reduction with potassium in DME and observed at -70° , indicated that the odd electron was localized in one phenyl ring (97). This work was questioned, and it has been suggested that the workers were, in fact, observing the ESR spectra of trialkylphenylsilane radical anions arising from decomposition reactions of the

TABLE VI
ELECTRON SPIN RESONANCE DATA FOR SILAACENAPHTHENE AND SILAPHENALENE
RADICAL ANIONS^a



Compound	a_1	a_2	a_3	$a(\text{Si—H})$	Conditions
XXXII (R = H)	1.75	0.40	5.50	2.30	$e^-/\text{DME}, -75^\circ$
	1.45	0.55	5.45	2.10	$e^-/\text{THF}, -75^\circ$
	2.75	0.80	5.45	2.75	$e^-/\text{DMF}, \text{RT}$
XXXII (R = Me)	2.60	1.00	5.30	—	$e^-/\text{DME}, -75^\circ$
	2.55	1.20	5.35	—	$e^-/\text{THF}, -75^\circ$
	2.70	1.15	5.25	—	$e^-/\text{DMF}, \text{RT}$
	2.50	1.10	5.15	—	$e^-/\text{MeCN}, \text{RT}$
XXXIV (R = H)	3.15	0.90	5.40	3.15	$e^-/\text{DME}, -75^\circ$
	2.90	0.85	5.30	2.90	$e^-/\text{THF}, -75^\circ$
	3.15	0.80	5.30	3.15	$e^-/\text{DMF}, \text{RT}$
	2.75	0.75	5.35	2.75	$e^-/\text{MeCN}, \text{RT}$
XXXIV (R = Me)	2.80	1.05	5.40	—	$e^-/\text{DME}, -75^\circ$
	2.35	1.30	5.30	—	$e^-/\text{THF}, -75^\circ$
	2.90	1.05	5.25	—	$e^-/\text{DMF}, \text{RT}$
	2.50	1.15	5.40	—	$e^-/\text{MeCN}, \text{RT}$

^a Reproduced from Makarov *et al.* (101).

primary anion radicals (see Section III, B, 1,a) (135). The radical anion of diphenyldimethylsilane has been reported to be localized (97); delocalized at all temperatures (135); and localized at low temperatures, $< -70^\circ$, and rapidly exchanging at higher temperatures, $> -40^\circ$ (91, 138). The discrepancies in these reports may be related to differences in solvents, counterions, or temperatures. However, much of the confusion in the earlier literature is apparently related to the fact that the fairly general phenomenon of temperature- and solvent-dependent electron exchange between aromatic rings in polyaryl systems had been overlooked.

The bridging silicon in polyphenyl silanes separates practically independent π -systems (18). However, temperature-dependent ESR spectra attributed to electron exchange between the aryl substituents have been

observed for the radical anions of tetraphenylsilane (124), diphenyldimethylsilane, and bis-(*p*-trimethylsilylphenyl)dimethylsilane (138, 92), and diphenyldiethylsilane (125, 124). In general, low temperatures favor localization of the unpaired electron in one phenyl ring; the electron-exchange rate between the aryl rings being slow on the ESR time scale, $\nu_e < 10^6 \text{ sec}^{-1}$ (68); characterized by a large coupling constant for the para proton of the ring. As the temperature is raised, rapid exchange between the phenyl rings is observed, characterized by a coupling constant for the para protons of the phenyl rings which is approximately $1/n$ times that observed for the slow exchange conditions, where n is the number of phenyl rings bonded to the central atom (135, 138). Table VII shows some typical results. Unfortunately, many aryl silane radical anions decompose rapidly at low temperatures. Only localized spectra have been observed for a large number of polyaryl silane radical anions (138), and a generalized study of exchange phenomena in these systems has not been possible.

The electron-exchange phenomenon is not limited to organometallic radical anions. It has been observed for diphenylmethane (109, 123, 125), triphenylmethane (108), and spirobifluorene radical anions (19, 64). In the spirobifluorene systems, evidence that is consistent with spin localization being a result of the association of the radical anion with its alkali metal counterion has been presented. Since this association is solvent-dependent, decreasing solvent polarity favors spin localization (64). It is reasonable to anticipate that the counterion association should also be temperature dependent with lower temperatures favoring increased association between the radical anion and its counterion, giving rise to localized spectra (138, 120). However, this explanation would not apply to radical anions generated electrolytically, in which case the electron-transfer mechanism must operate "through space" between the aromatic rings (138). There is ample evidence for spin density at silicon or germanium in arylsilane or germane radical anions (see Section III, B); but these metalloid elements do not seem to provide a ready pathway for electron transfer between the rings. Theoretical treatments for electron transfer in anion radical of the general type $\text{Ar}-\text{X}-\text{Ar}^-$ do predict a temperature dependence for the electron transfer (68).

4. Theoretical and Bonding Considerations

a. Hückel Correlations. The McConnell relationship $a_i = Q\rho_i$, where a_i is the observed hyperfine coupling constant, ρ_i is the spin density, and Q is a proportionality constant (104), provides a direct correlation between the experimental ESR spectra of radicals and theoretical bonding descriptions.

In the simple Hückel treatment, the $(\text{CH}_3)_3\text{M}$ group ($\text{M} = \text{Si}$ or Ge) is treated as a heteroatom substituent with a vacant p orbital on the aryl π -system. The parameters describing the "heteroatom" are the Coulomb integral α_{M} , and the resonance integral, β_{CM} , which are scaled in terms of the resonance integral of a "normal" aromatic C—C bond (127): $\alpha_{\text{M}} = \alpha_{\text{O}} + h_{\text{M}}\beta_{\text{O}}$; $\beta_{\text{CM}} = k_{\text{CM}}\beta_{\text{O}}$. Some workers have found it necessary to include a measure of the inductive effect of the substituent on the contiguous ring carbons in order to account for the spin density distribution. In the Hückel model, a substituent less electronegative than carbon decreases the Coulomb integral, α_{CM} , of the ring carbon to which the substituent is bonded; the degree of such perturbation is assumed to be proportional to h_{M} (127): $\alpha_{\text{CM}} = \alpha_{\text{O}} + \delta h_{\text{M}}\beta_{\text{O}}$, where δ is known as the auxiliary inductive parameter.

In the Hückel model, the spin density ρ_i , is taken as the square of the coefficient for the i th atom in the orbital to which the unpaired electron is assigned, C_{i0}^2 .

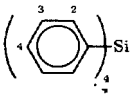
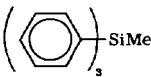
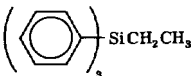
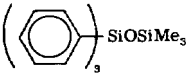
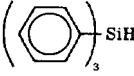
Using a perturbation treatment, McLachlan has derived an expression for spin densities that corrects the Hückel spin densities for configuration interaction effects (106): $\rho_i = C_{i0}^2 - \lambda \sum \pi_s C_{os}^2$, where λ is a constant and π_s is an atom-atom polarizability.

Curtis and Allred used the experimental spin densities for a series of trimethylsilyl- and trimethylgermyl-substituted biphenyl anion radicals to evaluate "best values" of the heteroatom parameters for the trimethylsilyl and trimethylgermyl substituents, based on a Q value of 28. The values thus obtained were $h_{\text{Si}} = -1.20$, $h_{\text{Ge}} = -1.05$, $k_{\text{CSi}} = 0.450$, $k_{\text{CGe}} = 0.300$, when an auxiliary inductive parameter of 0.10 was assumed. Excellent agreement with experimental data was obtained using these parameters. The C—M π -bond orders found by the model were approximately 0.18 for silicon and 0.13 for germanium (20). Subsequent application of the same parameters to silicon- and germanium-substituted polyphenylene and naphthalene systems gave similar results (1).

Using a similar approach, Evans and co-workers obtained values of $h_{\text{Si}} = -1.50$, $k_{\text{CSi}} = 0.55$, $\delta = 0.15$ for a series of trimethylsilyl-substituted naphthalene radical anions based on a Q value of -26.1 (49). For phenyltrimethylsilylacetylene radical anion, the values of the heteroatom parameters that gave the best fit of the Hückel calculated spin densities with "experimental" values, using a Q value of 28, were $h_{\text{Si}} = -1.3$, and $k_{\text{CSi}} = 0.65$ when a δ value of 0.1 was assumed. A resulting C—Si π -bond order of about 0.3 is obtained (43).

Using $Q_{\text{CH}} = -27$ G for alkenylsilane radical anions and $Q_{\text{CH}} = -27$ G for aryl and naphthyl silanes, Gerson, Heinzer and Bock found that values of $h_{\text{Si}} = -1.50$ and $k_{\text{CSi}} = 0.55$ gave satisfactory agreement with spin distribution in the radical anions. In these calculations the auxiliary

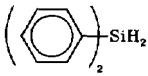
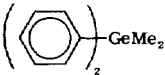
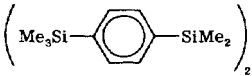
TABLE VII
POLYPHENYL GROUP IV ANION RADICALS

Anion radical	a_2	a_3	a_4	Electron exchange	Conditions	Ref.
	3.0	1.0	8.0	Slow ^a	K/DME, -70°	97
	1.1	0.4	2.26	Rapid	e^- /DMF, -65°	75
	0.8	—	2.2	Rapid	K/THF, -40°	124
			8.0	Slow	K/THF, -140°	
	0.80	<0.10	2.12	Rapid	K/THF, DME, -76° to -10°	135
	1.15	1.05	2.80	Rapid	K/DME, HMPA, -70°	35, 41
	2.8	1.2	8.4	Slow ^a	K/DME, -70°	97
	1.01	0.19	2.76	Rapid [0.26(SiCH ₃)]	K/THF, DME, -76°	135
	3.0	1.2	8.2	Slow ^a	K/DME, -70°	97
	2.7	1.2	8.1	Slow ^a	K/DME, -70°	97
	2.9	1.1	8.2	Slow ^a	K/DME, -70°	97

$\left(\text{C}_6\text{H}_5 \right)_2 \text{SiMe}_2$	2.94	1.47	8.56	Slow	NaK/MTHF, DME, -80°	91, 138
	1.37	—	4.25	Rapid	or e^-/THF , -80°	
	1.50	0.20	4.21, 4.11	—	$>-40^\circ$, Me_2O , DME	
	1.44	0.34	4.15	Rapid [0.17(SiCH ₃)]	K/DME, -78° K/THF, DME, -76°	120 135
$\left(\text{C}_6\text{H}_5 \right)_2 \text{Si}(\text{CH}_2\text{CH}_3)_2$	1.5	0.4	4.35 =8.	Rapid Slow	K/DME, THF?, R. T. -100°	125, 124
$\left(\text{Me}-\text{C}_6\text{H}_4 \right)_2 \text{SiMe}_2$	3.24	1.55	9.32(CH ₃)	Slow	e^-/MTHF , DME, -130° to -80°	138
$\left(\text{Me}_3\text{C}-\text{C}_6\text{H}_4 \right)_2 \text{SiMe}_2$	3.28	1.65	—	Slow	e^-/MTHF , DME, -130° to -70°	138
$\left(\text{Me}_3\text{Si}-\text{C}_6\text{H}_4 \right)_2 \text{SiHMe}$	1.76	1.86	—	Slow	e^-/THF , DME, -110° to -100°	138
	0.9	0.9	—	Rapid	-70° to -50°	138
$\left(\text{Me}_3\text{Si}-\text{C}_6\text{H}_4 \right)_2 \text{SiMe}_2$	1.76	1.76	—	Slow [8.84(Si—H)]	e^-/THF , -100° to -80°	138
$\left(\text{C}_6\text{H}_5 \right)_2 \text{SiHMe}$	3.15	1.58	8.50	Slow [7.13(Si—H)]	e^-/THF , -120° to -90°	138

(continued)

TABLE VII—(Continued)

Anion radical	a_2	a_3	a_4	Electron exchange	Conditions	Ref
	3.29	1.78	8.35	Slow 6.03 (Si—H)	e^- /THF, -120° to -90°	138
	2.33	1.46	7.87	Slow	e^- /THF, -100° to -60°	138
(PhSiMe ₂) ₂	2.90	0.90	8.16	Slow	-95°	138
(PhSiMe- <i>t</i> -Bu) ₂	3.36	1.51	8.08	Slow	-95° to -70°	138
	1.74	1.74	—	Slow	e^- /THF, -100° to -50°	138

^a It has been suggested that all of these might, in fact, be PhSiMe₃[•] due to decomposition of the initially produced radical and methyl abstraction from DME (135). See text.

inductive parameter was neglected (60). The best agreement with experiment was obtained using a McLachlan-type relation with $\lambda = 0.4$. The McLachlan spin densities thus obtained were used to relate the ^{29}Si coupling constants, a_{Si} , to the spin populations ρ_{Si} and ρ_{Ci} of the silicon and the substituted carbon, Ci, respectively. For the relation $a_{\text{Si}} = Q_{\text{Si}}\rho_{\text{Si}} + Q_{\text{CiSi}}\rho_{\text{Ci}}$, a value of about 20 G was found for the spin polarization term Q_{CiSi} , but the direct term Q_{Si} appears to be not significantly different from zero (60). This latter finding may result from the fact that the various spin polarization contributions to Q_{Si} cancel because of similar magnitudes and opposite signs. In addition, Q_{Si} may be smaller than values observed for the second-row elements because of the diffuse character of the 3d or 3p AO in which ρ_{Si} resides (60).

The most extensive correlation of ESR results for trimethylsilyl-substituted aromatic radical anions with Hückel MO calculations to date is the work of Sipe and West (118, 119). The optimum heteroatom parameters for both the simple Hückel treatment and the Hückel-McLachlan treatment, using a $Q_{\text{CH}} = -28$ G, for Me_3Si were as follows: Hückel, $h_{\text{Si}} = -2.00$, $k_{\text{CSi}} = 0.70$; Hückel-McLachlan, $h_{\text{Si}} = -1.80$, $k_{\text{CSi}} = 0.70$, $\lambda = 0.30$. The values for Me_3Ge were as follows: Hückel, $h_{\text{Ge}} = -1.45$, $k_{\text{CGe}} = 0.40$; Hückel-McLachlan, $h_{\text{Ge}} = -1.40$, $k_{\text{CGe}} = 0.40$; $\lambda = 0.10$ (118). We have found in our work that these parameters give excellent agreement with experimental spin densities for trimethylsilyl- and trimethylgermyl-substituted aniline radical cations (29, 28).

For the series of trimethylsilylaryl radical anions, Sipe and West found that the silicon-methyl proton ESR splitting, although not related to the π density on silicon alone or to the density on the aromatic carbon to which silicon is bonded, may be related to a combination of the spin densities by the relation:

$$a_{\text{SiCH}_3}^{\text{H}} = \rho_{\text{Ci}}Q_{\text{CiSiCH}_3}^{\text{H}} + \rho_{\text{Si}}Q_{\text{SiCH}_3}^{\text{H}}$$

with $Q_{\text{CiSiCH}_3}^{\text{H}} = 1.90$ and $Q_{\text{SiCH}_3}^{\text{H}} = -2.35$ G (118). This is in contrast to an earlier suggestion by other workers that a simple relationship

$$a_{\text{SiCH}_3}^{\text{H}} = \rho_{\text{Ci}}Q_{\text{SiCH}_3}^{\text{H}}$$

with $Q_{\text{SiCH}_3}^{\text{H}} = 1.0$ applied for the anion radical of 1,4-disilacyclohexadiene and related compounds (80).

b. Semiempirical Calculations. The biggest disadvantage of simple Hückel calculations is that they include an initial assumption of π -bonding between the Group IV element and the aromatic system, and only the extent of this π -bonding is varied. The excellent agreement with experiment, which has been obtained in applying Hückel calculations to

Group IV unsaturated molecules, indicates the significance of π -bonding effects. However, no differentiation of the orbitals involved in the bonding and, thus, no differentiation between d-orbital effects and hyperconjugative effects is possible. Recently, several groups have performed semiempirical SCF-MO calculations which, to some extent, overcome this difficulty (29, 85, 112).

Good agreement between experimental hyperfine coupling constants and CNDO/2 calculated π -spin densities has been obtained for Group IV-substituted *N,N*-dimethylaniline radical cations (29) and radical anions (85). Although the dimethylamino group is generally a strong π -electron donor, precluding the reduction of most anilines to radical anions of sufficient stability for detailed study (62), the substitution of an organosilyl substituent at any ring position enhances the electron affinity of the *N,N*-dimethylanilines to the point where metal or electrolytic reduction to radical anions is feasible (84, 86, 87). In the radical anions, the electron-donating effect of the dimethylamino group is significantly diminished, a phenomenon that, according to CNDO/2 calculations is due to repulsion between the excess electron density in the reduced benzene π -system and the nitrogen lone pair electrons (84, 86). The organosilyl substituent is the major influence on the spin distributions in the aniline radical anions (85, 86).

On the basis of complete neglect of differential overlap (CNDO/2) calculations which include silicon p and d orbitals in the basis set, the effect of the trimethylsilyl substituent is due to electron withdrawal by the interaction of both the silicon p and d orbitals with the aromatic π -system (85). In as much as the silicon p orbitals are primarily involved in the σ and σ^* orbitals of the trimethylsilyl group, interaction of the silicon p orbitals with the π -system amounts to a hyperconjugative, $\pi \rightarrow \sigma^*$, electron withdrawal (85).

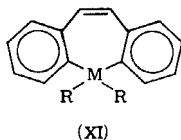
In an attempt to differentiate between hyperconjugative effects and d-orbital effects for silyl substituents, the radical anions of a series of *p*-silyl-substituted *N,N*-dimethylanilines, *p*-SiH_{*n*}Me_{3-*n*}-C₆H₄NMe₂ (*n* = 0-3), were investigated (86). As methyl groups on silicon are replaced by hydrogen, the electron-withdrawing effect of the silyl substituent increases to the extent that the spin distribution in *p*-silyl-*N,N*-dimethylaniline radical anion approaches that for *p*-nitro-*N,N*-dimethylaniline radical anion. The trend follows the improving match in energy between the silyl σ^* -group orbitals and the π^* -levels in the aniline which occurs as methyls are replaced by hydrogens (86). In the CNDO/2 calculations for these radicals, the silicon d π -orbital spin density remains essentially constant for the series, whereas the $p\pi$ -spin density increases with increasing number of hydrogens on silicon. Although the CNDO/2

calculations indicate that both the silicon p and d orbitals of π -symmetry interact with the aniline π -system, only the variation in the silicon p-orbital parameters follow the experimentally observed trends. It appears that the variation in the interactions of the σ^* -levels of the silyl substituents with the aniline π -system, and not the variation in d-orbital interactions, account for the trends observed (86, 87).

The CNDO/2 calculations have recently been carried out for the methylphenylsilane anion radicals using an spd basis set, and the calculated spin density values agree well with experimental hyperfine coupling constants. The CNDO method seems to overestimate the role of d orbitals, and the partial charges on hydrogen atoms attached to silicon. The calculated bond orders for the bond between silicon and the ring carbon atom decrease as methyl groups on silicon are replaced by hydrogen atoms in the radical anions. The opposite trend is calculated for the neutral molecules (112).

While the jury is still out on the nature of the acceptor orbitals on silicon, the bulk of the evidence seems to be pointing to d-orbital interactions being most important when silicon is bonded to electronegative elements with available lone pairs. Silicon's interaction with organic π -systems appears to be predominantly hyperconjugative in nature. In systems where molecular symmetry permits differentiation between d-orbital and hyperconjugative effects, such as 9-silafluorenes, hyperconjugative effects are observed (110a).

The ESR spectra of the stable radical anions of the dibenzometallopins (XI; M = Si, $R_2 = \text{Ph}_2$, PhMe, and Me_2 ; and M = Ge, $R_2 = \text{Ph}$), show little sensitivity to the metal atom or metal atom substituent that lies in a node of the occupied molecular orbital (117a). In these radical anions, only d orbitals on the metal have the appropriate symmetry to interact with the orbital occupied by the unpaired electron.



C. Polysilanes

One of the clearest indications of the presence of acceptor orbitals on silicon is the ability of polysilanes to be reduced to radical anions (73). Although early work assigned the structure $(\text{Me}_2\text{Si})_6^-$ to the radical anion produced by reduction of dodecamethylcyclohexasilane (73), subsequent investigations showed that cyclic $(\text{Me}_2\text{Si})_5$, $(\text{Me}_2\text{Si})_6$, and $(\text{Me}_2\text{Si})_7$ all

give rise to the $(\text{Me}_2\text{Si})_5^-$ anion radical when the reduction is carried out with alkali metals. The radicals $(\text{Me}_2\text{Si})_6^-$, $(\text{Me}_2\text{Si})_5^-$, and $(\text{Me}_2\text{Si})_4^-$ may be obtained by low-temperature electrolytic reduction (15). The order of electron affinity, determined by competitive reductions, is $(\text{Me}_2\text{Si})_4^- \sim (\text{Me}_2\text{Si})_5^- > \text{benzene} > (\text{Me}_2\text{Si})_6^- > (\text{Me}_2\text{Si})_7^-$ (15). It is intriguing that, for the anion radicals, $(\text{Me}_2\text{Si})_5^-$ is more stable than $(\text{Me}_2\text{Si})_6^-$, whereas, for the neutral precursors, the opposite order of stability is observed (137).

Consistent with the fact that the electronic spectral transitions of $(\text{Me}_2\text{Si})_5$ lie at lower energy than for $(\text{Me}_2\text{Si})_6$ (15), the ESR results suggest that the lowest unoccupied molecular orbital (LUMO) lies at lower energy for the five-membered ring than for the cyclohexasilane compound. A possible explanation is that the overlap of atomic orbitals contributing to the π^* -type unoccupied orbital in the cyclopolsilanes is improved when the rings are nearly planar. Distortions from planarity would increase in the order $(\text{Me}_2\text{Si})_4 \sim (\text{Me}_2\text{Si})_5 < (\text{Me}_2\text{Si})_6 < (\text{Me}_2\text{Si})_7$, consistent with the experimental observations (137).

It has been observed that alkali metal reduction of a linear polysilane $(\text{Me}_2\text{Si})_n$, where $n > 50$, leads to cleavage of the chain and cyclization of the fragments, eventually giving the ESR spectrum of $(\text{Me}_2\text{Si})_5^-$, although in the report the spectrum was assumed to be that of the dodecamethylcyclohexasilane anion radical (13). The same report indicated that the ESR spectrum of linear decamethyltetrasilane anion radical consisted of 11 to 13 components with a splitting constant of 2 G, which is about 3 times larger than the splitting observed for the methyl protons of the cyclic polysilanes (13).

Several substituted permethylcyclopolsilanes have been reduced to anion radicals and studied by ESR. Included among the compounds were $\text{Si}_5\text{Me}_9\text{R}$ (where $\text{R} = \text{H}, \text{Ph}, \text{PhCH}_2, \text{Me}_3\text{Si}, \text{PhMe}_2\text{Si}$) and $\text{Si}_6\text{Me}_{11}\text{R}$ (where $\text{R} = \text{H}, \text{Ph}, \text{PhCH}_2$, and Me_3Si). All of the compounds form anion radicals in which the unpaired electron appears to be delocalized over the polysilane ring, except for $\text{Si}_6\text{Me}_{11}\text{Ph}$, where the phenyl ring is reduced (92). The ESR results are listed in Table VIII. The six-membered cyclopolsilane anion radicals were all unstable, decomposing in most cases to $(\text{Me}_2\text{Si})_5^-$, except for the silyl-substituted cyclopentasilane radical anions, which decompose by loss of the silyl substituent to give $\text{Si}_5\text{Me}_9\text{H}^-$ (92).

D. Other Group IV Compounds

1. Acylsilanes

The radical anions of acetyl trimethylsilane, isobutyroyltrimethylsilane (83) and benzoyltrimethylsilane (63), have been prepared by metal

TABLE VIII
POLYSILANE RADICAL ANION ESR DATA


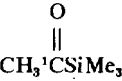
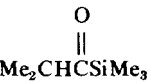
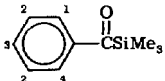
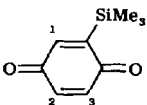
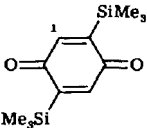
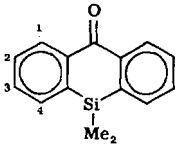
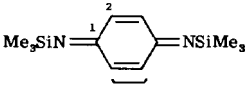
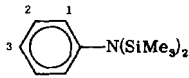
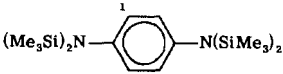
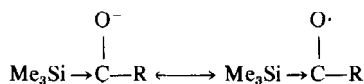
Anion radical	$a(\text{CH}_3)$	$a(^{13}\text{C})$	$a(^{29}\text{Si})$	$a(\text{other})$	Conditions	Ref.
Cyclo-(Me ₂ Si) ₄	0.67	20.97	—	—	e^-/MTHF , DME	137
Me ₃ Si(SiMe ₂) ₂ SiMe ₂	2.0	—	—	—	NaK/DME, -30° to -50°	13
Cyclo-(Me ₂ Si) ₅	0.53	16.03	6.10	—	e^-/MTHF , DME, -120° to -80°	15
	0.53	16.06	6.13	—	NaK/MTHF, G	15
Cyclo-(Me ₂ Si) ₆	0.49	14.60	—	—	$e^-/\text{Me}_2\text{O}$, DME	15
Cyclo-(Et ₂ Si) ₆	—	14.2	4.45	—	NaK/DME, -30° to -50°	13
Cyclo-Si ₅ Me ₉ -H	0.51, 1.02	13.3, 24.4	—	14.1(Si-H)	e^-/THF , -95°	92
Cyclo-Si ₅ Me ₉ -SiMe ₃	0.56	—	—	—	e^-/THF , -95°	92
Cyclo-Si ₅ Me ₈ -(SiMe ₃) ₂	—	23.1, 17.2	—	—	e^-/THF , -95°	92
Cyclo-Si ₅ Me ₉ -Ph	0.51	14.7	—	—	e^-/THF , -90°	92
	0.54	17.0	—	—	e^-/THF , -60°	92
Cyclo-Si ₅ Me ₉ CH ₂ Ph	0.54	16.1	—	—	e^-/THF , -95°	92
Cyclo-Si ₆ Me ₁₁ -H	—	—	—	13.4(Si-H)	e^-/THF , -110°	92
Cyclo-Si ₆ Me ₁₁ - 	Aryl ring reduced	—	—	7.65(2); 2.65(1)	e^-/THF , -95°	92

TABLE IX
OTHER ORGANOSILICON RADICAL ANIONS

Compound	a_1	a_2	a_3	a_4	$a(\text{SiCH}_3)$	$a(\text{other})$	Conditions	Ref.
	17.27	—	—	—	0.16	—	K/THF, DME, -90°	83
	3.68	—	—	—	0.17	—	K/THF, DME, -90°	83
	4.28	1.02	5.25	3.15	0.13	8.34(^{29}Si)	K/DME, -80°	63
	2.68	2.10	2.52	—	≤ 0.1	1.82(^{29}Si)	e^- /DMF, 25°	63
	2.79	—	—	—	≤ 0.1	1.51	e^- /DMF, 25°	63

	2.4	0.8	3.2	0.8	—	—	e^- /DMF, 25° or KNa/ DME, -75°	98
$\text{Me}_3\text{C}-\text{N}^1=\text{N}^2-\text{SiMe}_3$	10.85(N) 10.40	4.28(N) 4.57	—	—	—	—	Na/THF, 0° K/THF, 0°	93 93
$\text{Me}_3\text{Si}-\text{N}=\text{N}-\text{SiMe}_3$	6.62(N) 6.25	—	—	—	—	—	Na/THF, 0° K/THF, -80°	93 93
	4.02(N)	2.00	—	—	≤ 0.08	3.68(^{29}Si) 160(^{13}C)	K/DME, 25°	63
	5.1	5.7	≤ 0.5	—	≤ 0.1	—	K/DME, 25°	62
	5.43	—	—	—	≤ 0.1	$\leq 0.5(\text{N})$	K/DME, 25°	62

reduction in donor solvents at low temperatures. Their ESR spectra, when compared with their carbon analogs, indicate that the trimethylsilyl group favors spin rather than charge density on the carbonyl carbon, consistent with the $+I$ inductive effect of silicon (83):



Thus, the spin density in the phenyl ring in benzoyltrimethylsilane ketyl is 10–20% lower than in the aryl ring of the ketyl of acetophenone (63). It is also noteworthy that the coupling constants for the ortho protons in benzoyltrimethylsilane ketyl are not equivalent, clearly indicating restricted rotation about the acyl carbon, aromatic carbon bond in the ketyl (63). All of the reported acylsilane radical anions are unstable above -50° and couple to give new paramagnetic dimer spectra (83, 63). The dimers could conceivably arise from condensation of the ketyl with unreduced ketone (83). The electrolytic reduction of benzoyltrimethylsilane in DMF at room temperature leads directly to a mixture of the radical anions of benzaldehyde and benzil, without ever giving the spectrum of the original radical anion (63).

In the ESR spectra of some related trimethylsilyl benzoquinone derivatives, as with the ketyls, the spin density in the quinone ring increases for trimethylsilyl substitution and decreases for alkyl substitution, consistent with the electron-accepting ability of the trimethylsilyl group. This ability is also manifested in the reduction potentials of the compounds (63). The ESR data for the trimethylsilyl ketyls and for the trimethylsilyl benzoquinone anion radicals are summarized in Table IX.

2. Silicon–Nitrogen Compounds

The ESR spectra of radical anions of the trimethylsilyl derivatives of diimine (93), 1,4-benzoquinone diimide (63), and *N*-trimethylsilyl derivatives of aniline and *p*-phenylenediamine (62) have been obtained, and the data are summarized in Table IX. The results for all the systems illustrate the ability of the trimethylsilyl group to withdraw electron density from nitrogen. Its ability to delocalize π -spin population lies intermediate between alkyl groups and the phenyl ring (93, 63). The *N*-trimethylsilyl aniline and *p*-phenylenediamine radical anions represent the only known cases of aniline radical anions in which the odd electron occupies the antisymmetric π^* -orbital (62). Other systems in which this orbital might be anticipated to be lower in energy than the symmetric π^* -orbital have not been successfully reduced (83).

IV

TRANSITION METAL ORGANOMETALLICS

The ESR spectrum of the complex of *t*-butylphenyl ketyl with the $\text{Cr}(\text{CO})_3$ group, compared with the uncomplexed ketyl, shows decreased spin density in the aromatic ring. However, no splitting from the ^{53}Cr nucleus was observed (17).

Electron spin resonance has been used to investigate the steric effects in the paramagnetic anion chelates of molybdenum tetracarbonyl with 1,4-diazabutadienes of the type $\text{R}^1\text{N}=\text{C}(\text{R})\text{C}(\text{R})=\text{NR}^1$ ($\text{R} = \text{H}$ or Me ; $\text{R}^1 = \text{Me}$, PhCH_2 , CHMe_2 , cyclohexyl, and cyclopropyl). The nitrogen substituent is found to be held in an energetically higher conformation in the chelate than in the uncomplexed anion radical due to the additional metal ligand (56).

The almost encyclopedic investigations of Dessy and co-workers in the early 1960s into the electrochemical behavior of organometallic compounds showed that a vast majority do not undergo reversible one-electron reductions. The initially produced radical anions undergo rapid decomposition reactions, although in several cases ESR spectra of paramagnetic species were reported (23). In subsequent investigations, electrochemical reduction of thirty-five metal-acetylene complexes (26) and of twenty-seven bridged, bimetallic metal-carbonyl complexes (25) gave evidence for stable anion radical and dianion formation in many cases.

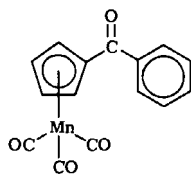
Processes for two-electron reductions, two sequential one-electron reductions with a radical anion intermediate, and reactions of dianions with unreduced parents to give radical anions were observed. Structural reorganization is occasionally observed, particularly in the case of $\text{Fe}(\text{CO})_2$ and $\text{Fe}(\text{CO})_3$ complexes (26). There appears to be little correlation between structure and electrochemical behavior. In general, the presence of metal-metal bonds in the substrate appears to correlate well with the ability to yield a stable radical anion on reduction. The lack of a metal-metal bond correlates, although poorly, with the ability to form radical cations (25). At present, the predictability of results from reduction in metal-carbonyl complexes is very low. The area remains one in which a great deal more work is needed.

Infrared spectral studies have been made for a large number of octahedral metal-carbonyl systems of the types $\text{LM}(\text{CO})_6$ ($\text{L} = \text{pyridine}$ and quinoline), $\text{L}_2\text{M}(\text{CO})_4$ [$\text{L}_2 = \text{ethylene diamine}$, $(\text{pyridine})_2$, and bipyridyl], $[\text{LM}(\text{CO})_4]_2$ ($\text{L} = \text{dimethylarsine}$ or dimethylphosphine ; $\text{M} = \text{Cr}$, Mo , and W), and $[\text{LFe}(\text{CO})_3]_2$ ($\text{L} = \text{SMe}$, PMe_2) before and after electrochemical reduction. The force constants for the carbonyl groups

decrease on reduction to the radical anions in a manner which is consistent with charge transmission primarily by a σ - rather than a π -effect (27). An extension of the studies to trigonal bipyrimidal olefin-iron tetracarbonyl systems shows that for these systems the charge transmission effects in the radical anions is predominantly a π -effect. The ESR spectra demonstrate high localization of the spin density in an orbital predominantly ligand in character (24).

In 1969, Elschenbroich and Cais reported the ESR spectra of several ferrocenyl anion radicals, including benzoyl, *p*-tolyl, *p*-carbomethoxybenzoyl, *p*-nitrophenyl, *p*-cyanophenyl, and nitroferrocene, prepared by electrolytic reduction in either acetonitrile or DMF (38). In general, the ferrocenyl group destabilizes the anion radicals compared to a phenyl substituent. When both groups are present, delocalization of the unpaired electron into the phenyl substituent is more extensive, and the ESR spectra resemble, for the most part, anion radicals of substituted aromatics. There is small spin density in the ferrocenyl moiety, which appears as small hyperfine couplings for the cyclopentadienyl protons ortho to the point of substitution (38).

In contrast to the ferrocenyl anion radicals (105, 21), benzoylcyclopentadienylmanganese tricarbonyl anion radicals (XII) show extensive delocalization over the entire system, with density predominantly centered on the phenyl ring, the ketonic CO, and the manganese atom (66, 67). For a variety of substituted cyclopentadienyl or phenyl rings, the anions show a large splitting from the ^{55}Mn nucleus and smaller splittings from the ortho and para substituents of the phenyl ring (66). Extended Hückel molecular orbital calculations gave good agreement between calculated and observed hyperfine coupling constants, and the change in spin density on varying the substituent positions shows that the major effect is electronic in nature (67).



(XII)

Radical cations of bisarene-transition metal complexes are produced relatively easily by oxidation (39). However, since the coordination of a neutral π -system to a metal is accompanied by a net metal \rightarrow ligand charge transfer, the energy of the LUMO is raised upon complex formation, and the electron affinity of the complex decreases (9). Thus, bisbenzenechromium could not be converted to a stable radical anion

(40). However, its isoelectronic unsymmetrical counterpart, π -cyclopentadienyl- π -cycloheptatrienylchromium(0) can be reduced to a stable anion radical (41). The orbital occupied by the unpaired electron has dominant ligand π character. It appears to consist of a combination of the antibonding e_2 MO's of the cyclopentadienyl (Cp) and cycloheptatrienyl (Tr) π -systems with about one-third Cp and two-thirds Tr, respectively (41). Reduction of π -cyclopentadienyl- π -methylcycloheptatrienylchromium leads to an unstable radical anion that decomposes by loss of the seven-membered ligand (41).

The reduction of "cobalt cluster" derivatives of the type $\text{RCCo}_3(\text{CO})_9$, where R = a variety of substituents including halogen, alkyl and aryl groups, and trimethylsilyl, gives radical anions of moderate stability. The ESR spectra of the anions indicate interaction between the unpaired electron and three equivalent cobalt nuclei. The coupling with cobalt is 36.0 ± 0.5 G with the exception of the trimethylsilyl compound for which it decreases slightly (102).

Organic nitroxides (136a, 5), nitroparaffins, and nitrolic acids (107) react with aqueous solutions of pentacyanocobaltate(II) salts to give alkyl pentacyanocobalt(III) nitroxide anion radicals, spin traps involving the formation of an N—Co bond (5).

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